Metal-organic frameworks: Metal-directed assembly and novel catalysts

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Northwestern University
and Argonne Natl. Lab

Acknowledgments

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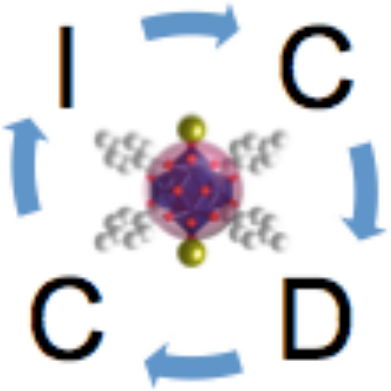
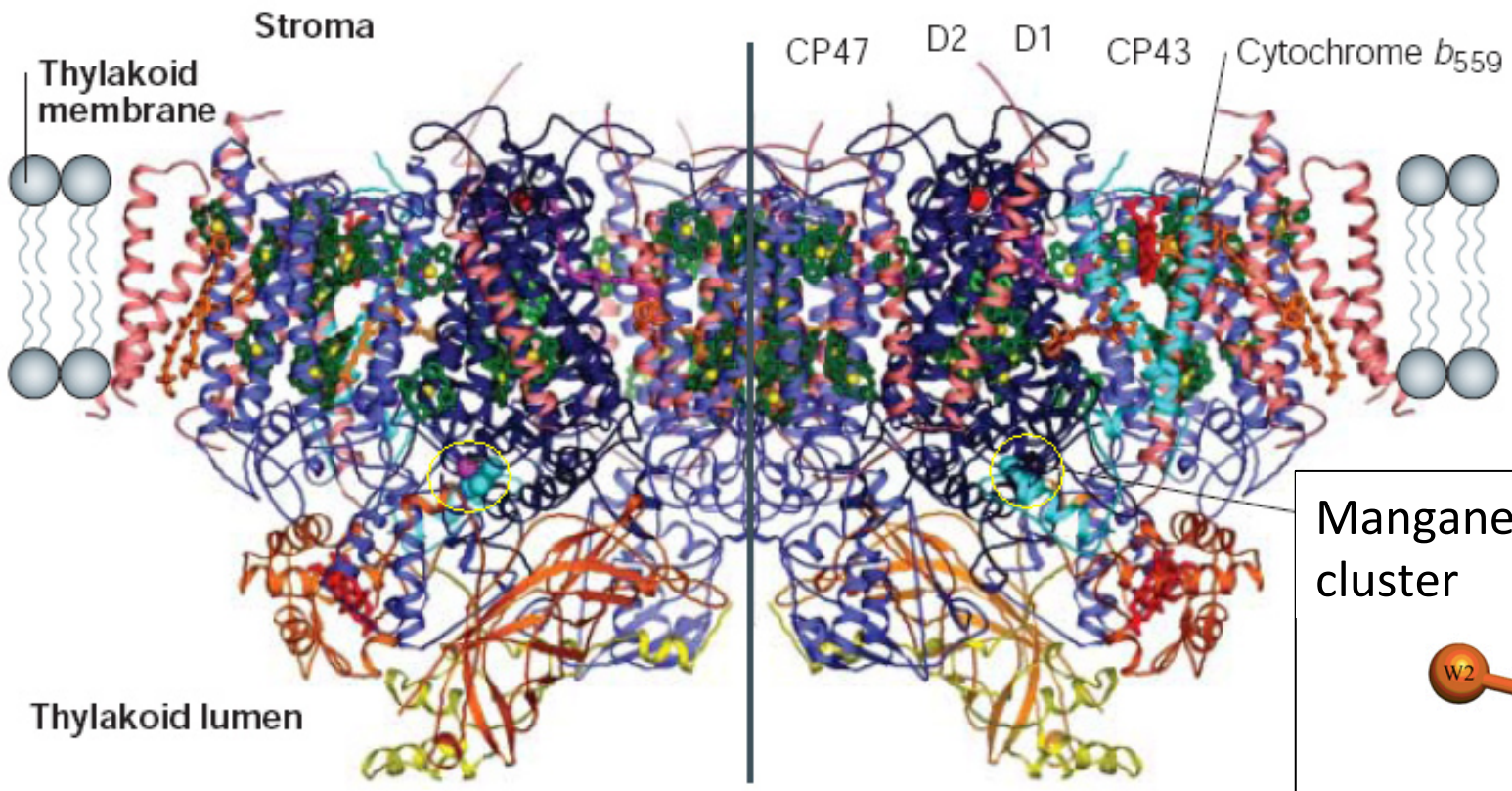
Acknowledgments



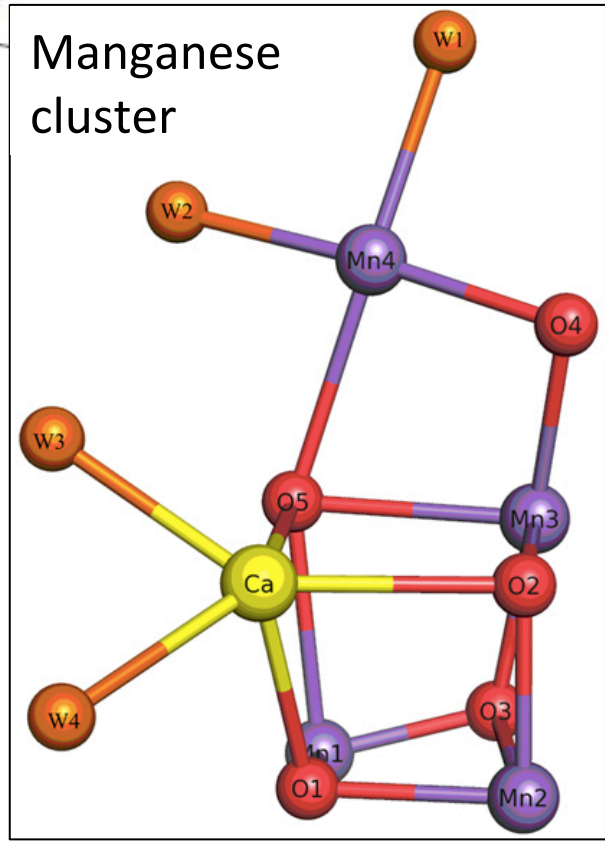
Arrays of metal-containing clusters for catalysis

- Water splitting: Electrocatalysis of water oxidation

- Heterogeneous catalysis of gas-phase reactions, e.g. alkene hydrogenation



Natan Nelson and Adam Ben-Shem, Nature Reviews Molecular Cell Biology 5:1 (2004)



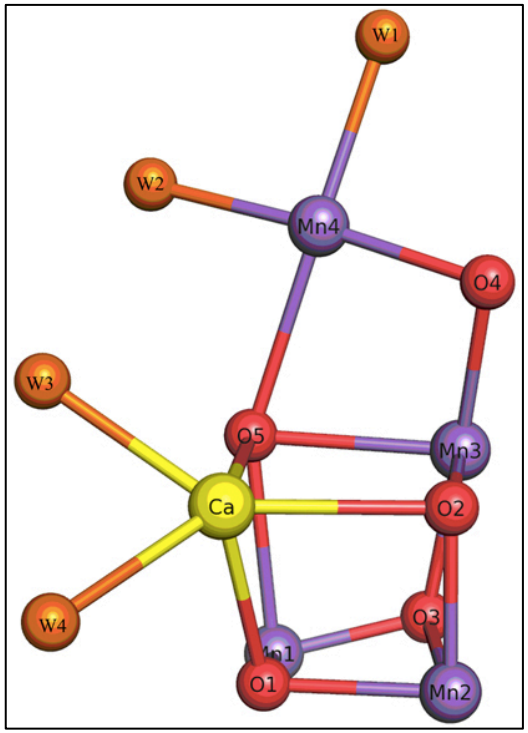
Photosystem II oxygen-evolving complex

From: Umena, et al., *Nature* **2011**, *473*, 55-61.

Artificial clusters as catalysts for O_2 or H_2 evolution

How can we:

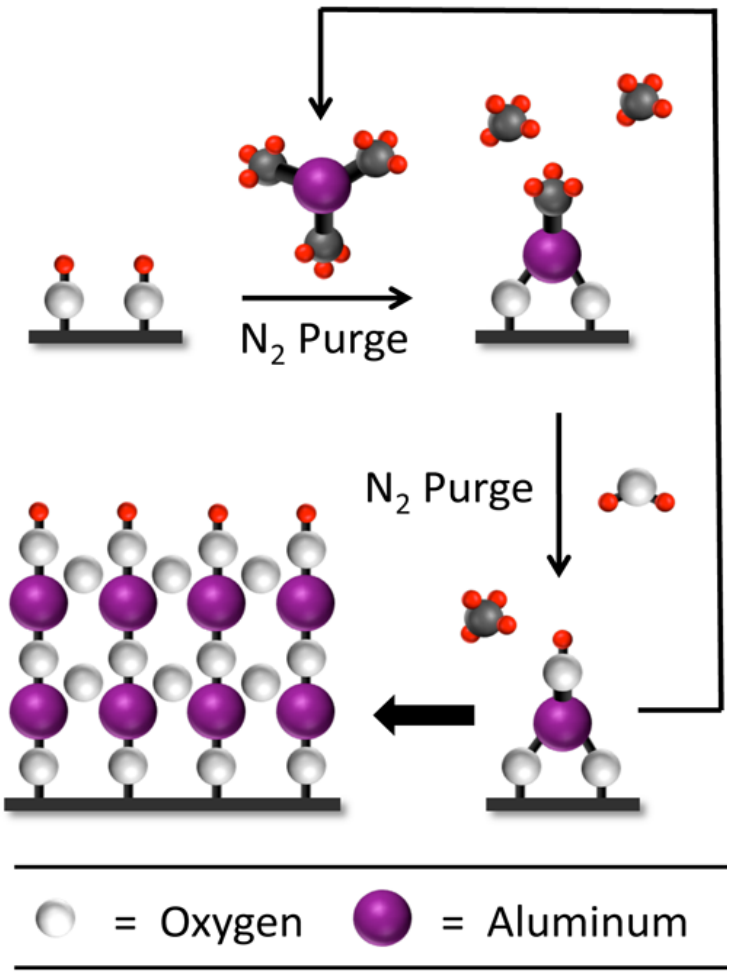
- create open sites?
- precisely control cluster size, shape, and composition?
- avoid cluster aggregation?
- address clusters photochemically?



From: Umena, et al., *Nature* **2011**, *473*, 55-61.

Synthesis Approach: Atomic Layer Deposition

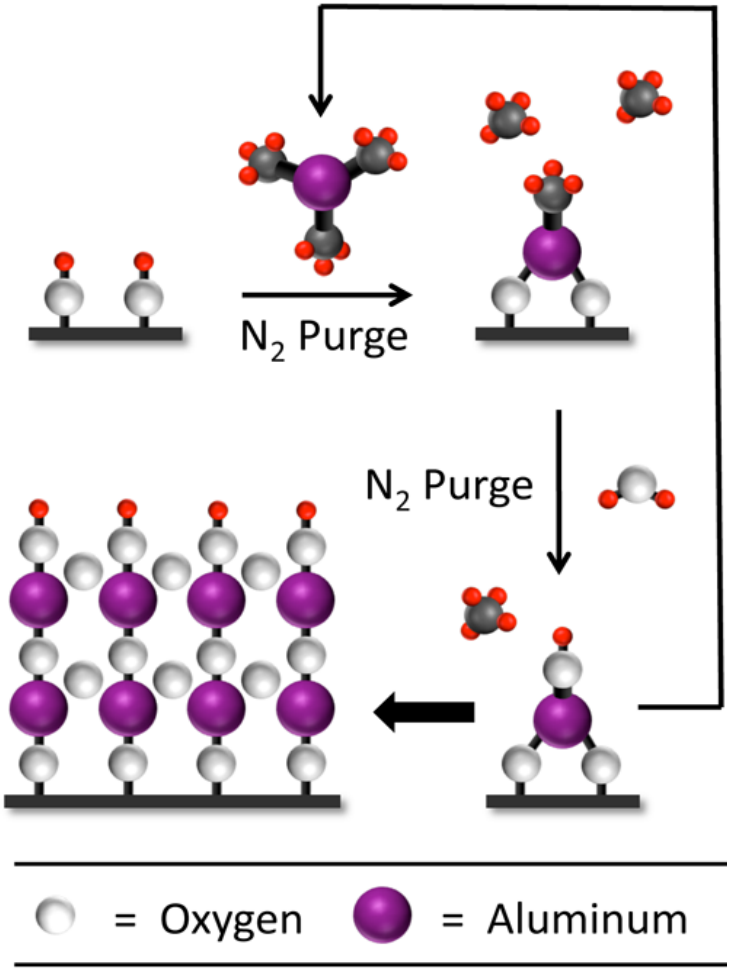
Thin-film ALD on a Surface



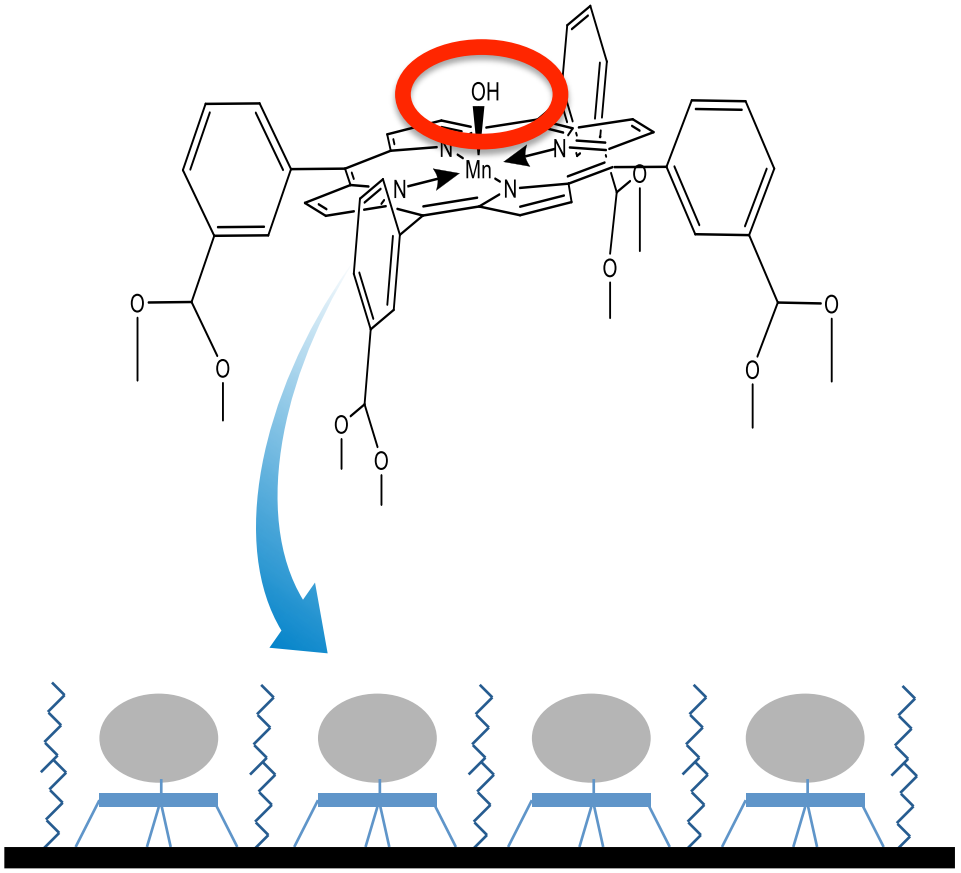
- Vapor phase → conformal
- 2 steps per cycle → self-limiting
- Repetition → error correction (pinhole elimination)
- Angstrom-level precision for average film thickness
- High reproducibility: automated

Synthesis Approach: Atomic Layer Deposition

Thin-film ALD on a Surface

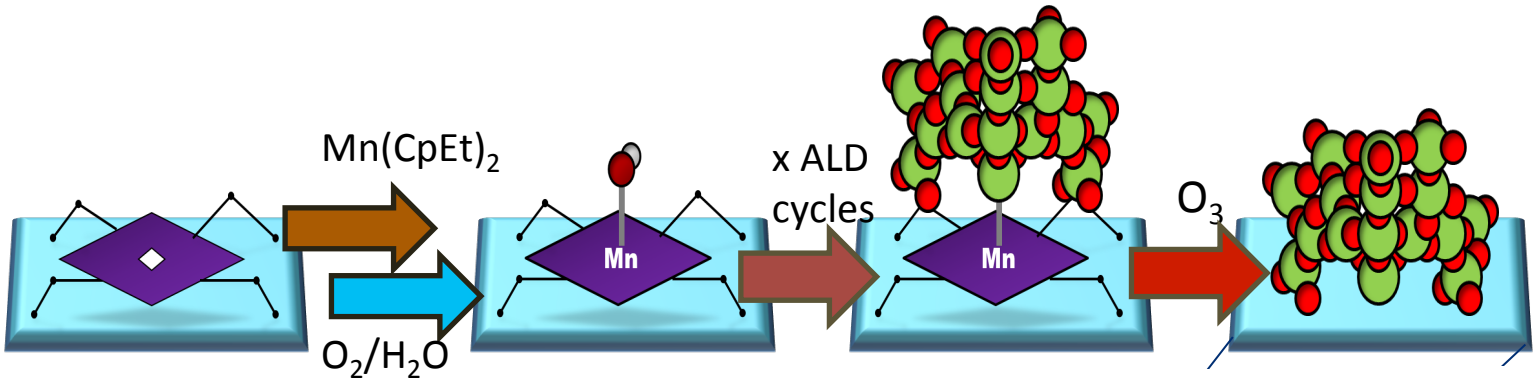


ALD on a Molecular Platform



electrode

ALD-like synthesis of electrode-supported arrays of metal-oxide clusters

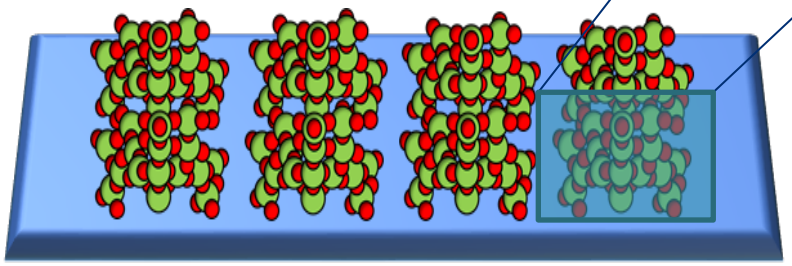


Free base porphyrin attached to electrode

Mn metalated with isolated OH nucleation site

ALD clusters of metal oxides

Porphyrin removal with ozone



Monodisperse array of metal-oxide clusters

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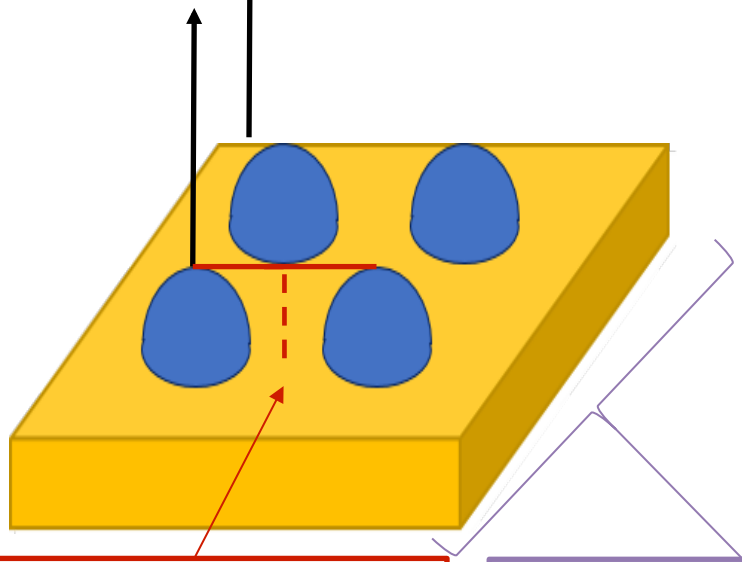
Using an analytic island growth model, the density and size of nucleation sites can be ascertained using "*in synthesis*" quartz-crystal microgravimetry (QCM)

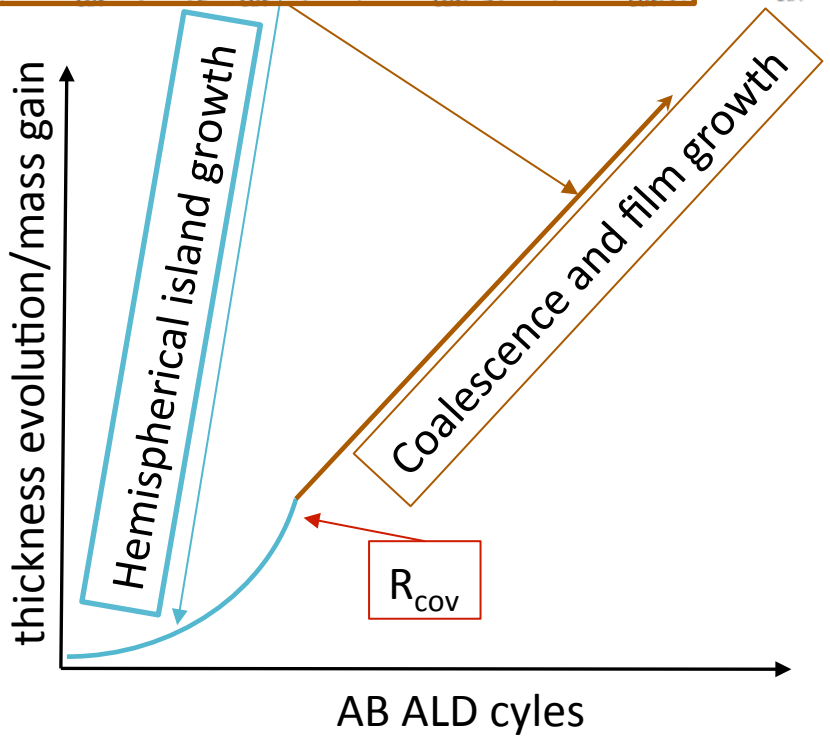
Evolution of thickness (μ) – growth of hemisphere normal to the surface



Radius of convergence (R_{cov}) – fixed radii before cluster coalescence.

Nucleation density (N_d) – density of nucleation at defect sites in the SAM film (pin holes).

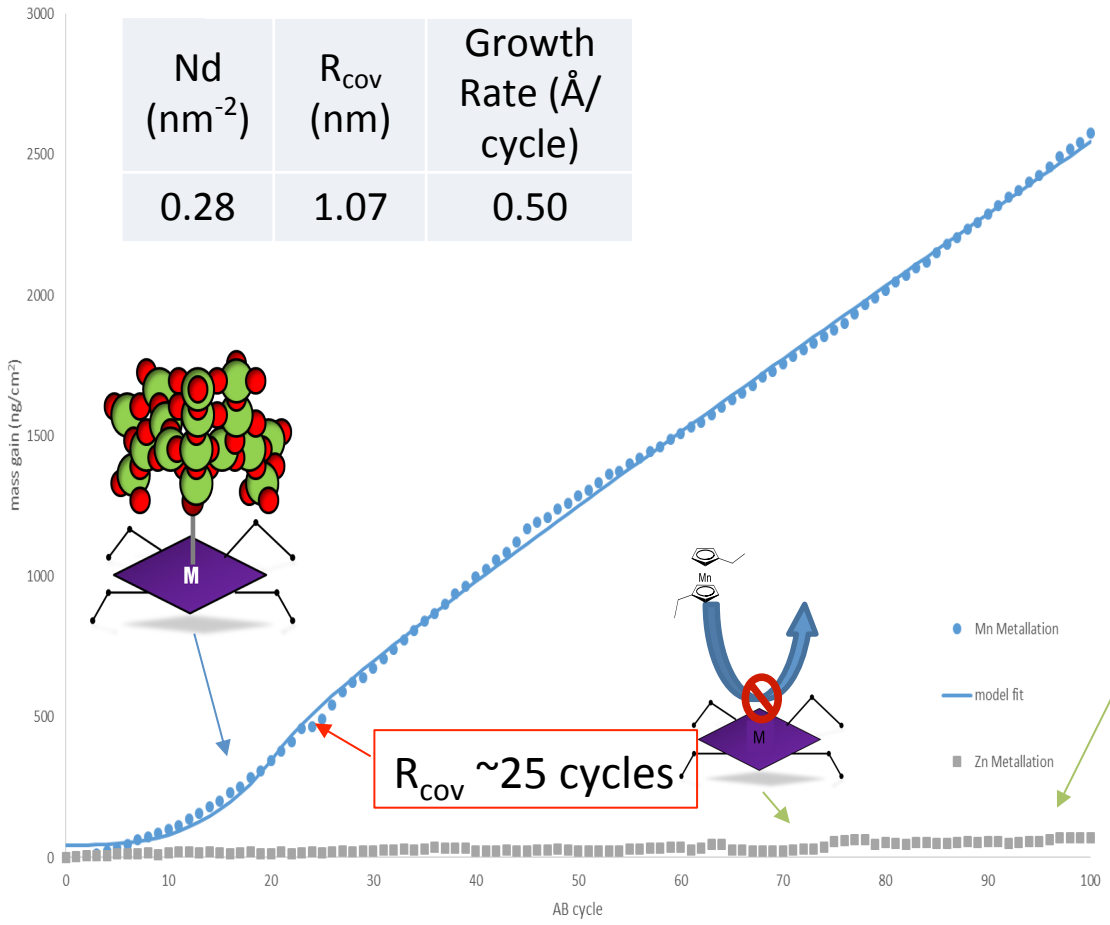
$$\mu = \begin{cases} (2/3)N_d\pi r^3, & r \leq R_{cov} \\ N_d\{\pi R_{cov}^2\sqrt{r^2-R_{cov}^2} + (\pi/6)[3R_{cov}^2 + (r-\sqrt{r^2-R_{cov}^2})^2](r-\sqrt{r^2-R_{cov}^2})\}, & r > R_{cov}, \end{cases}$$



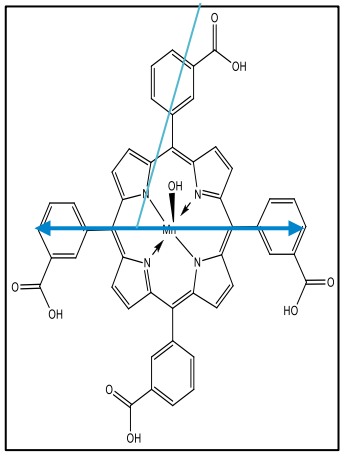
Nilsen, O.; *et. al. J Appl. Phys.* **2007**, 102, 024906

In-synthesis QCM shows successful growth of "$Mn(OH)_2$" clusters on metalated porphyrin platforms

Nd (nm^{-2})	R_{cov} (nm)	Growth Rate (Å/ cycle)
0.28	1.07	0.50



~1.5 nm → R_{cov} = 0.75 nm



With Zn porphyrin, no nucleation site is present. Experiment also shows that cluster growth at porphyrin interstitial sites is essentially nonexistent.

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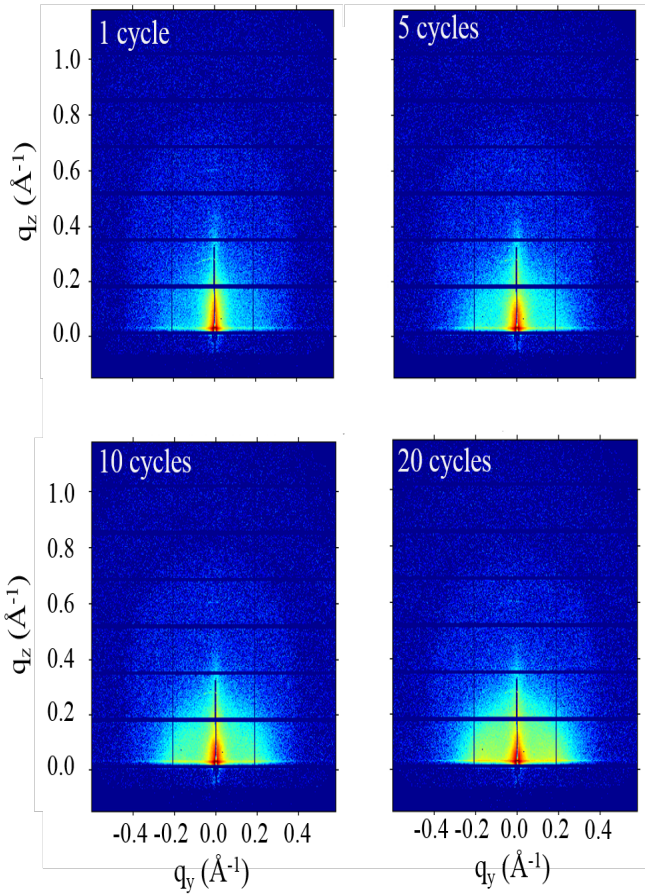
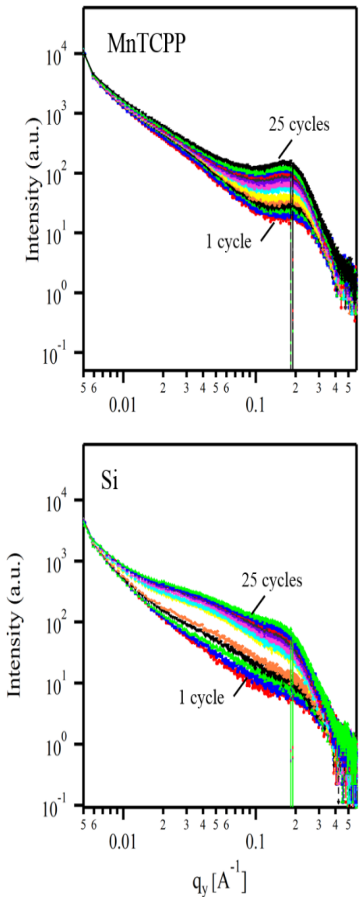
Figure 5 – GISAX scattering profile of MnO on porphyrin



- Preliminary GISAX in-situ scattering showing form factor evolution and inter-particle scattering
- Silicon platform shows less form factor evolution and minimal inter particle scattering

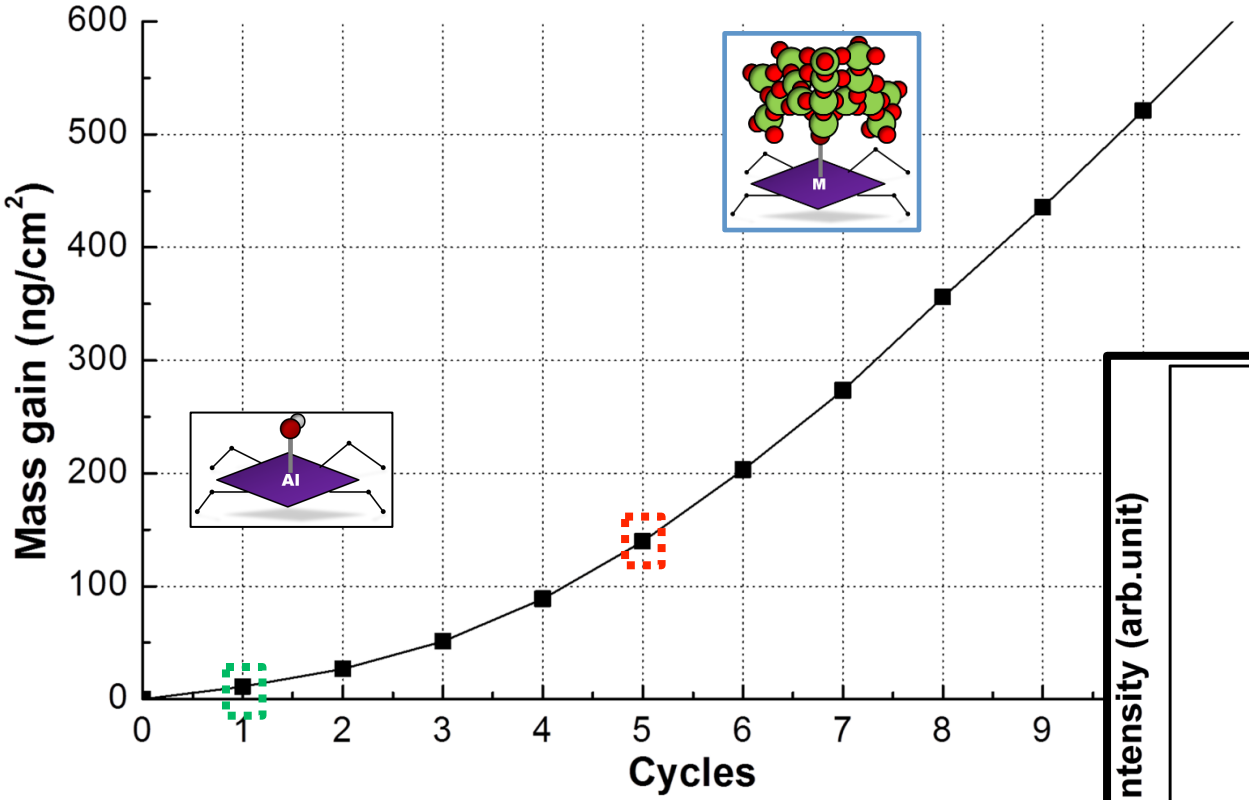
qy cut showing form factor of MnO clusters grown on porphyrin vs Si

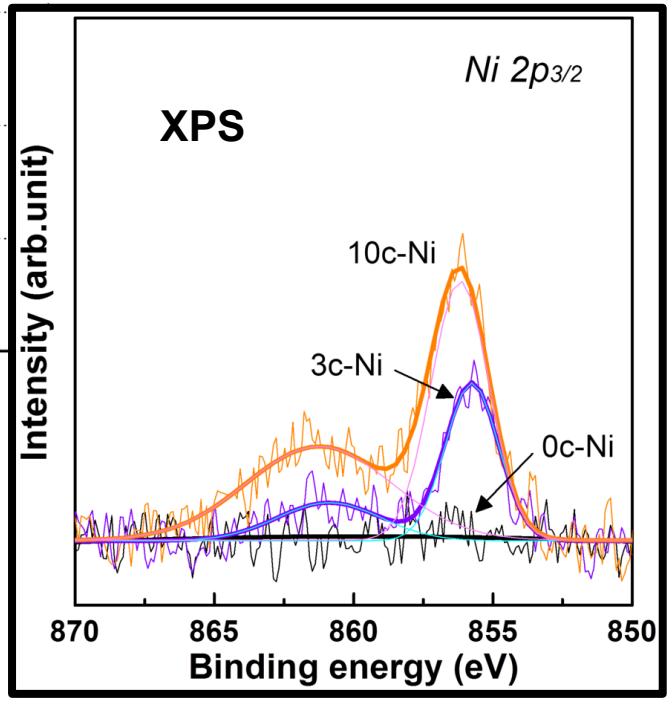


- In-plane cut shows clear feature with the porphyrin platform and not the silicon support
- Silicon platform shows only increase in intensity
- Porphyrin peak indicates a cluster - cluster distance of 5 angstroms

Similar idea: Nickel oxide cluster formation

ALD-QCM





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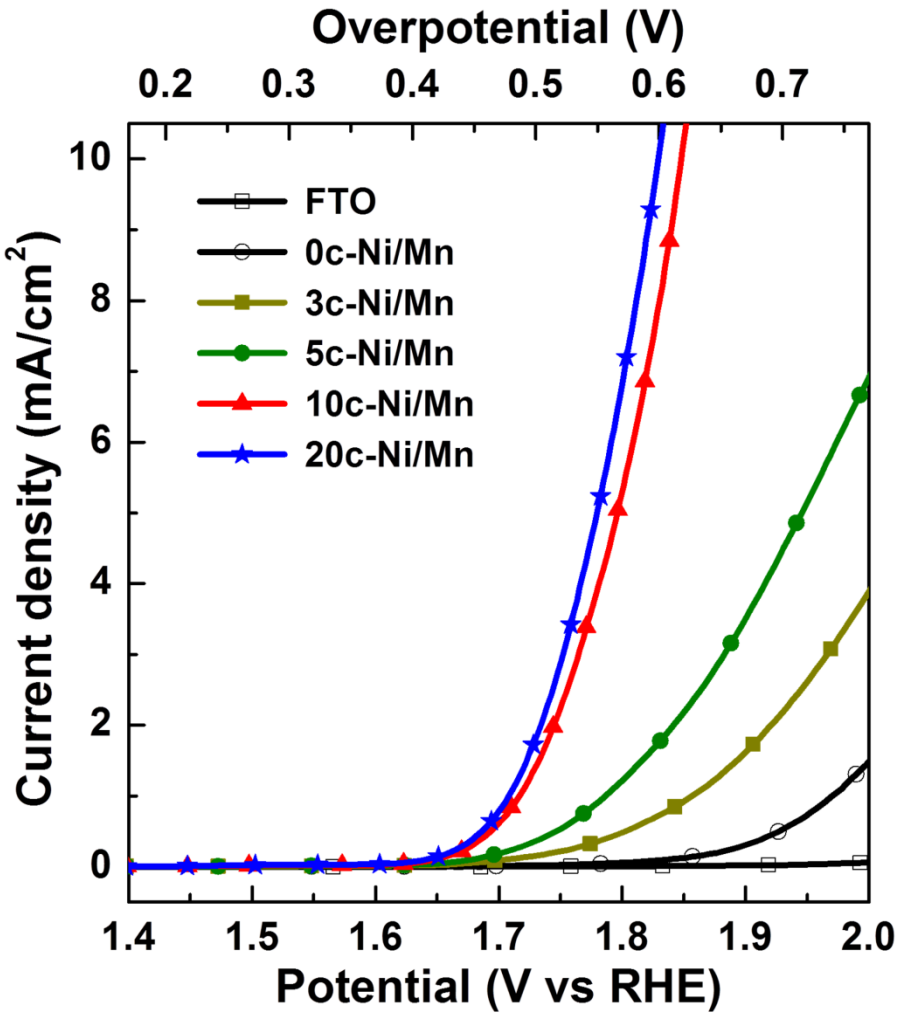
Does it work?
Electrochemical water oxidation by NiO clusters

Current density in alkaline electrolyte (1 M NaOH)



Differing numbers of ALD synthesis cycles

Does it work?
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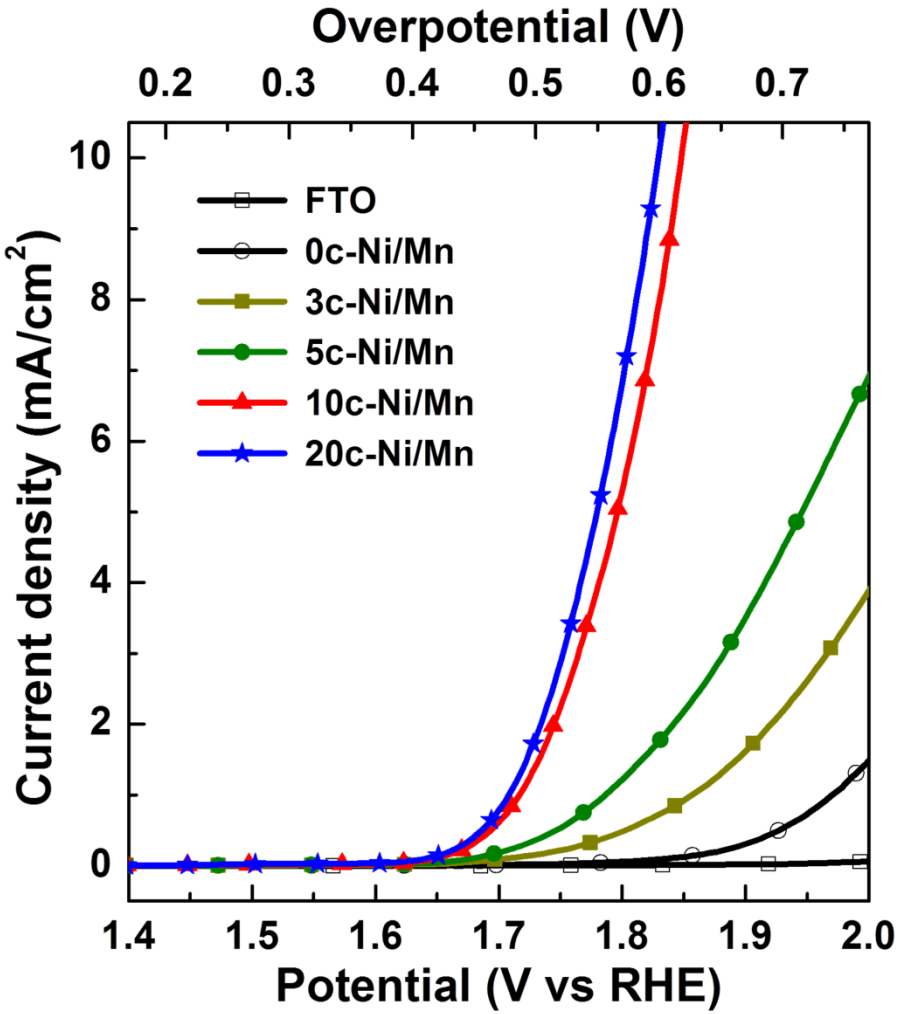

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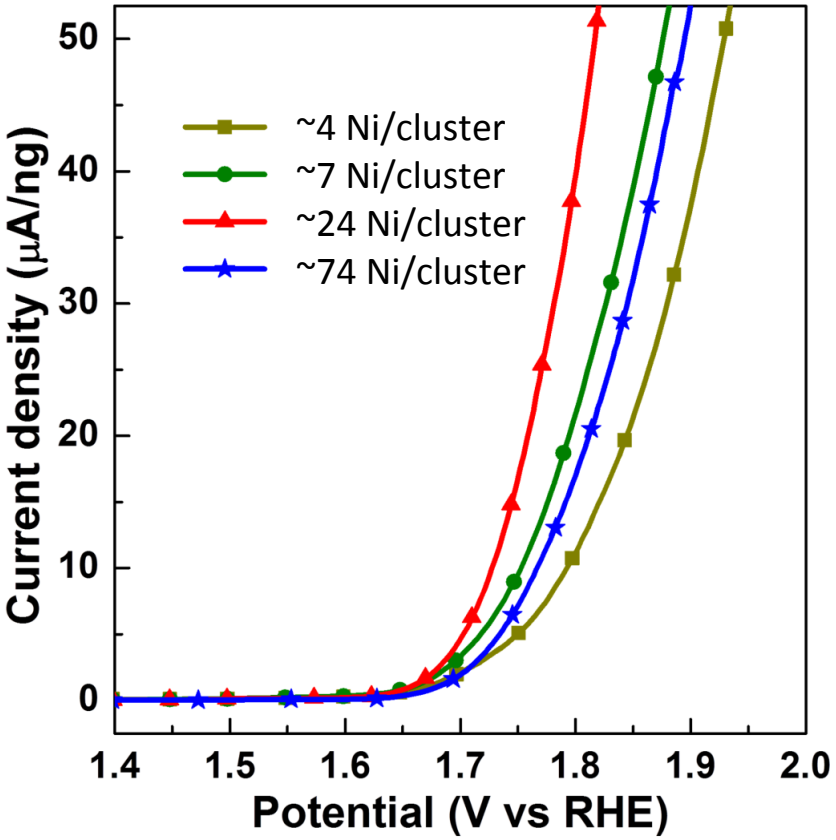
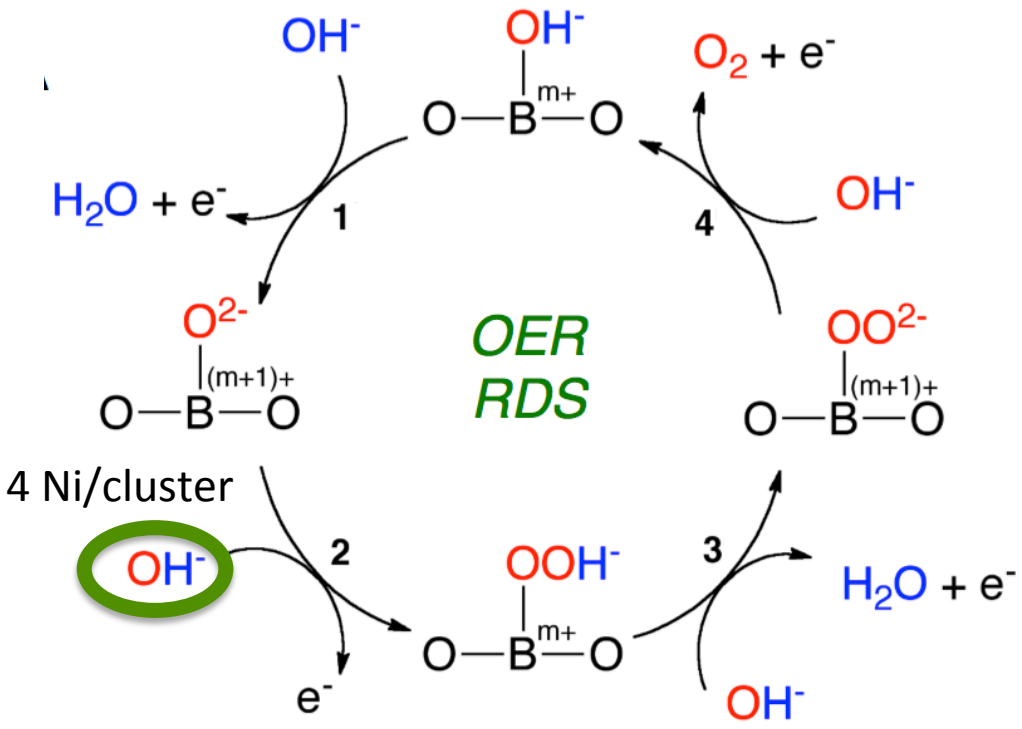


Normalized for cluster mass

Mechanistic Kinetics of Electrocatalysis

Tafel plots for oxygen evolution via nickel oxide clusters in 1 M hydroxide



56 mV Tafel slope →
β = 0.95 → 1 e^- transferred before rate-determining chemical step

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Mechanistic Kinetics of Electrocatalysis

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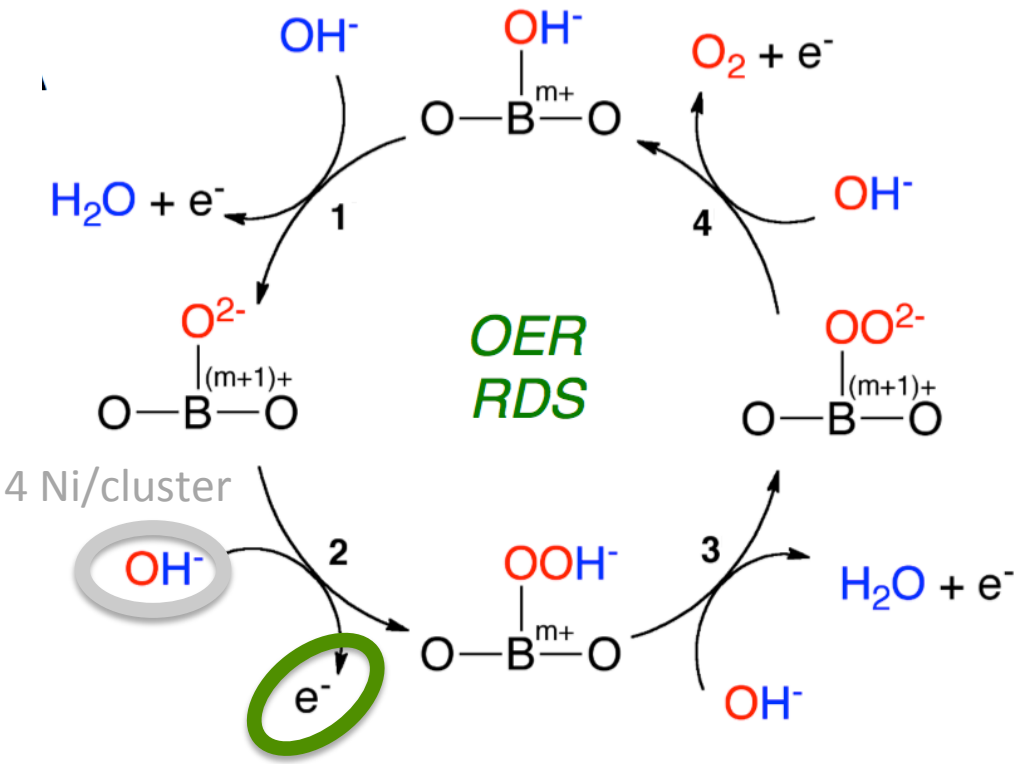

7 Ni/cluster

56 mV Tafel slope →
β = 0.95 → 1 e⁻ transferred before rate-determining chemical step

48 mV Tafel slope →
second e⁻ transfer (e-chem step) is rate determining

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Mechanistic Kinetics of Electrocatalysis

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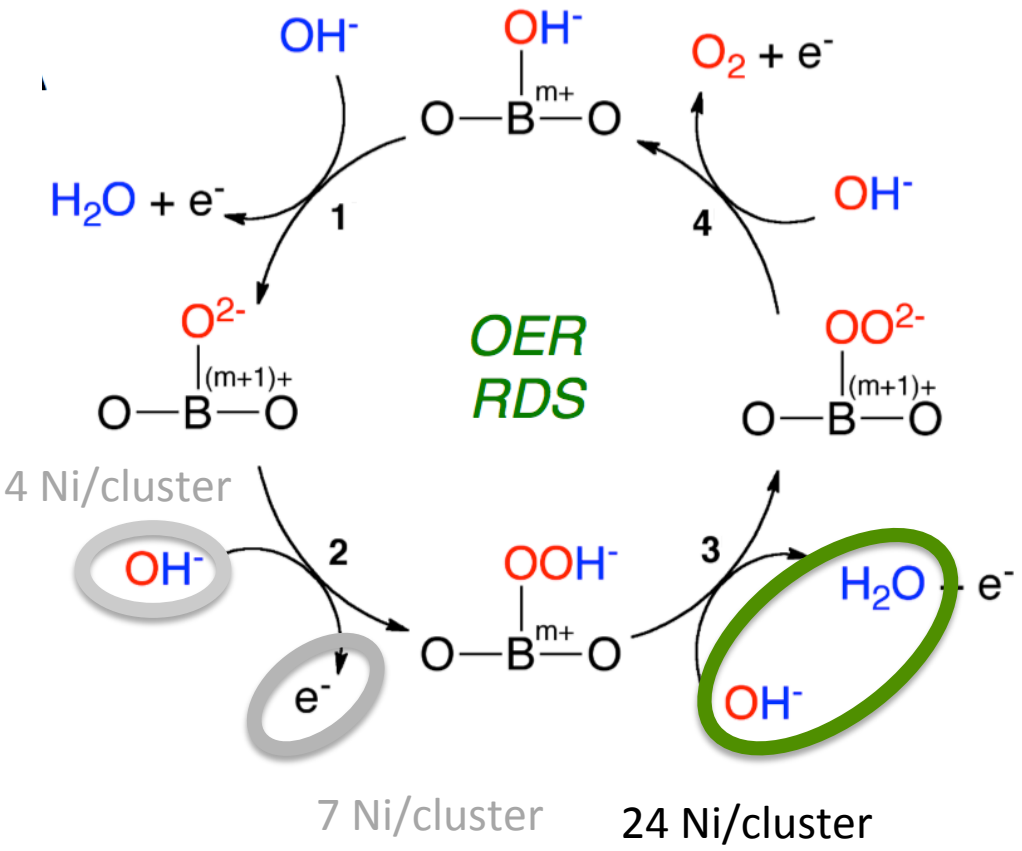

56 mV Tafel slope →
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48 mV Tafel slope →
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33 mV Tafel slope →
β = 1.8 → 2 e^- transferred before rate-determining chemical step

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Mechanistic Kinetics of Electrocatalysis

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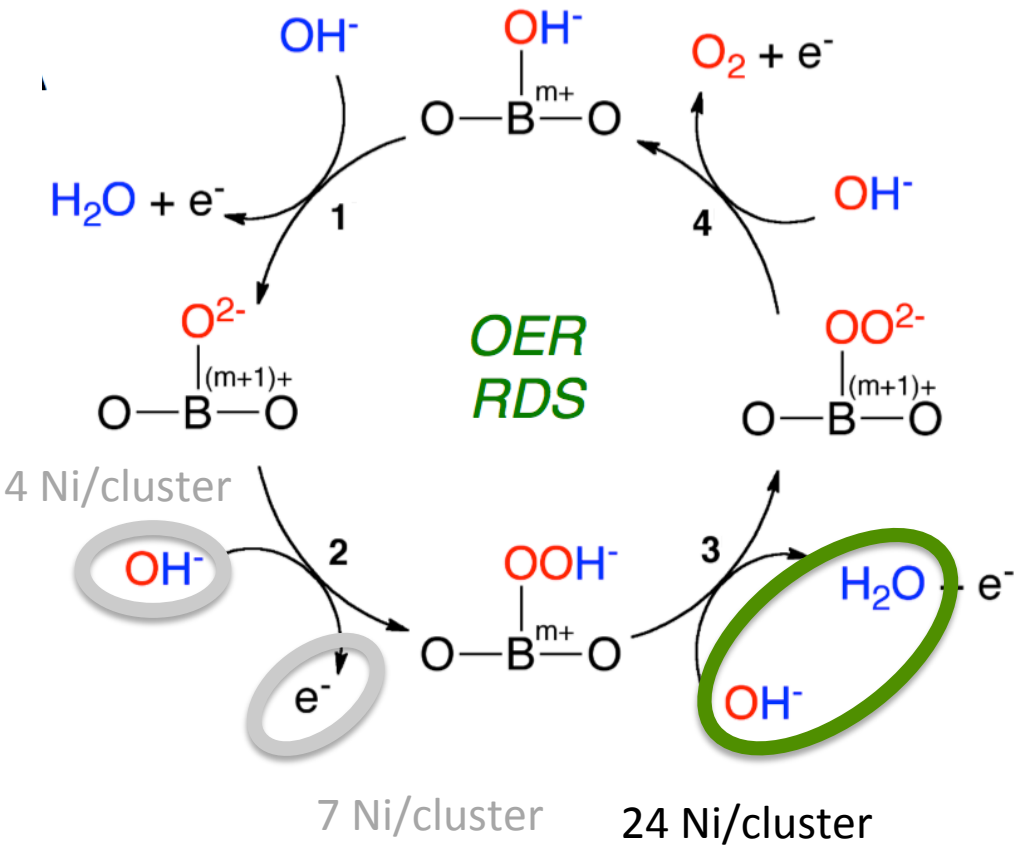

56 mV Tafel slope →
β = 0.95 → 1 e^- transferred before rate-determining chemical step

48 mV Tafel slope →
second e^- transfer (e-chem step) is rate determining

33 mV Tafel slope →
β = 1.8 → 2 e^- transferred before rate-determining chemical step

Rate-determining step is cluster size dependent!

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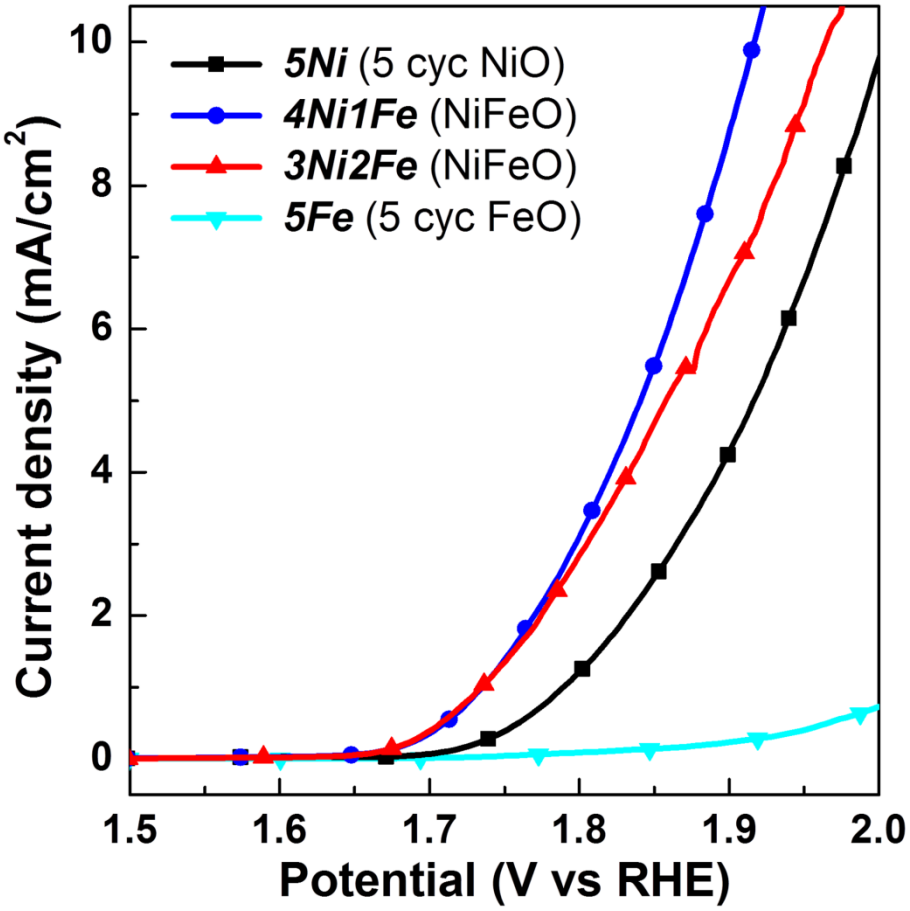
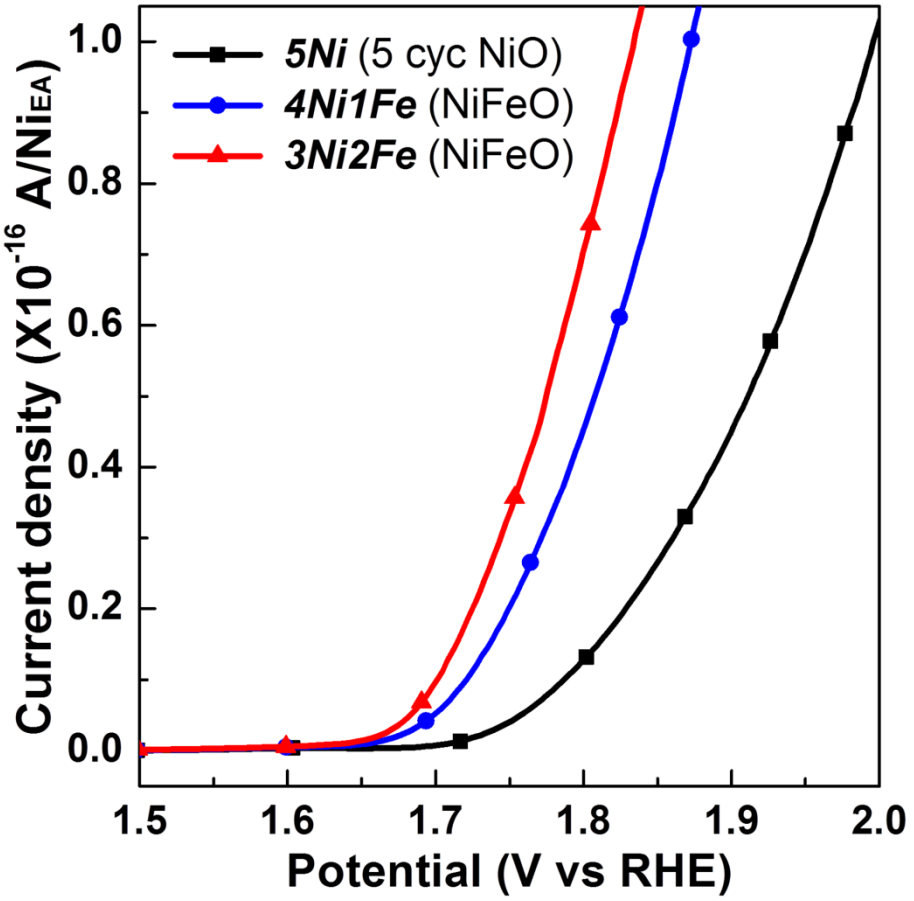
Mixed Metal-Oxide clusters are better catalysts Ni-Fe

Typical J-V curves vs Normalized curves for the number of electroactive sites





Questions

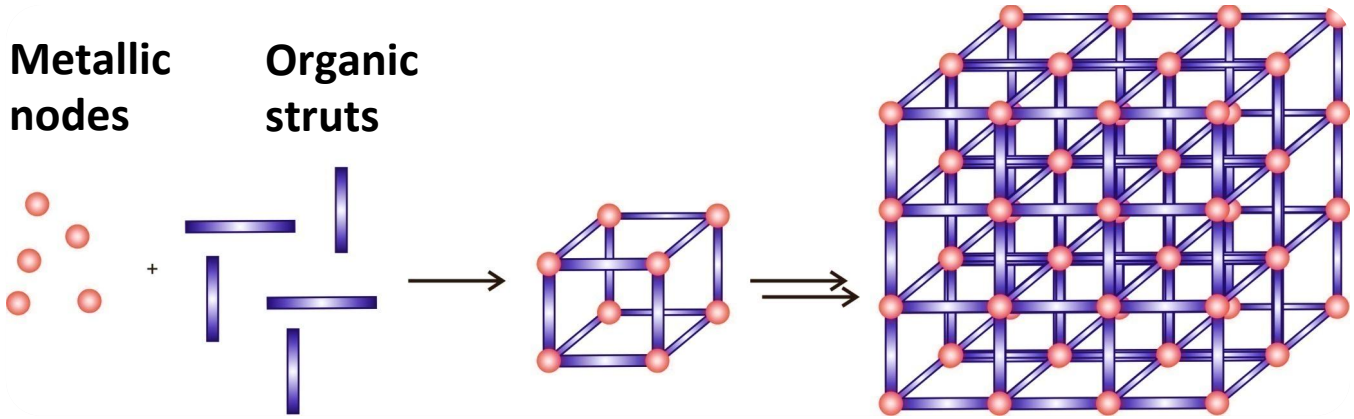
- Time-evolution of cluster structures?
- Potential dependence of cluster structures
- Distribution of different metals in mixed-metal clusters?
- Can we follow metal-oxygen bonding during the course of catalysis? Different cluster sizes allow us to stage different rate-determining steps.

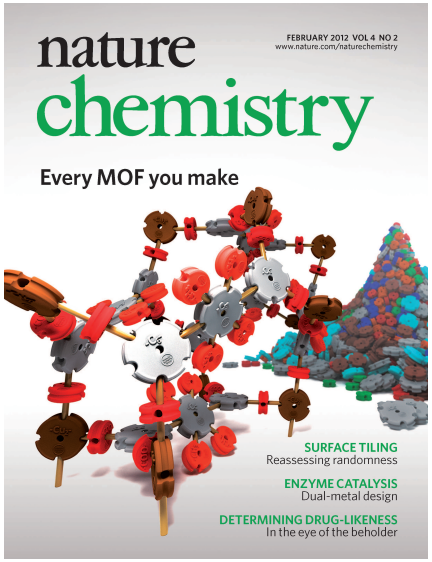
Arrays of metal-containing clusters for catalysis

- Water splitting: Electrocatalysis of water oxidation

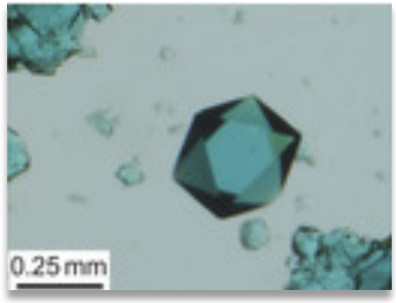
- Heterogeneous catalysis of gas-phase reactions, e.g. alkene hydrogenation

Metal-Organic Frameworks (MOFs)



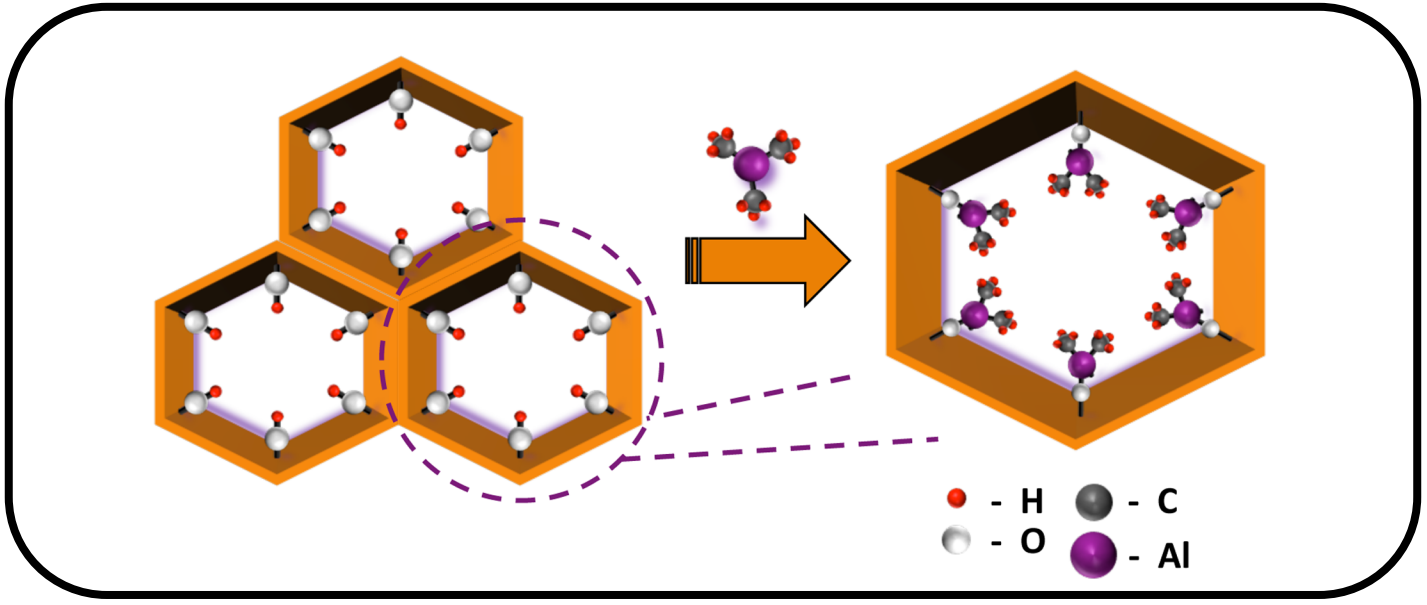


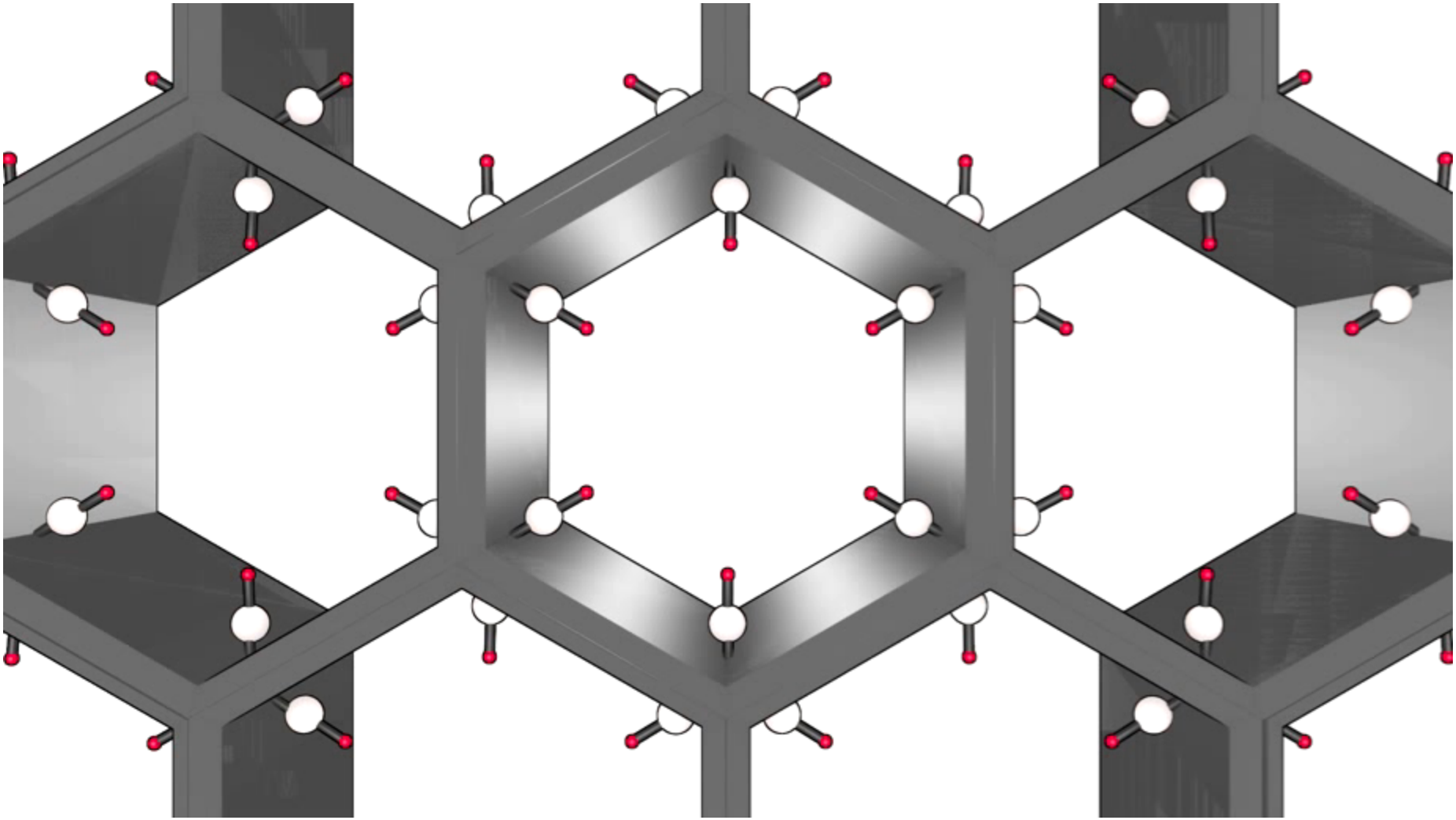
- Solvothermal synthesis; simple, scalable materials assembly
- Broad channel and pore size tunability
- Complete uniformity of channels
- Amenable to experimental structural characterization
- Amenable to computational modeling
- Enormous internal surface areas: up to 7,200 m^2/g



ALD In MOFs (AIM)

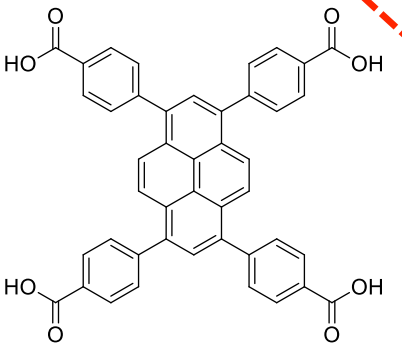
Global Hypothesis: *Coupling ALD and MOF (metal-organic framework) chemistry will allow us to develop hybrid materials with new and unique functions for materials related applications.*

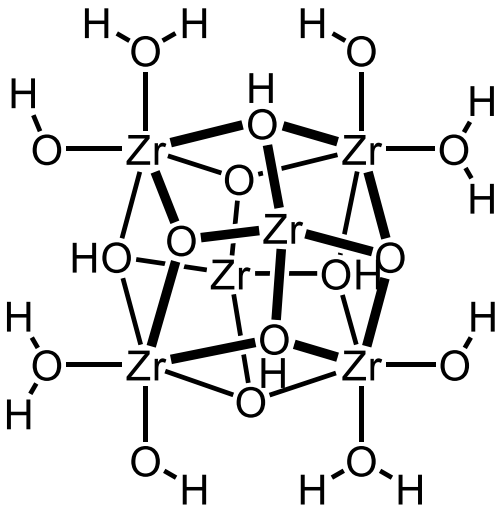


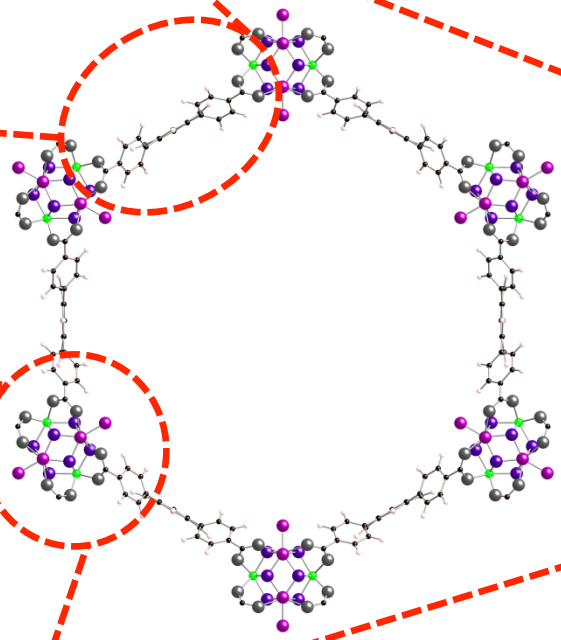


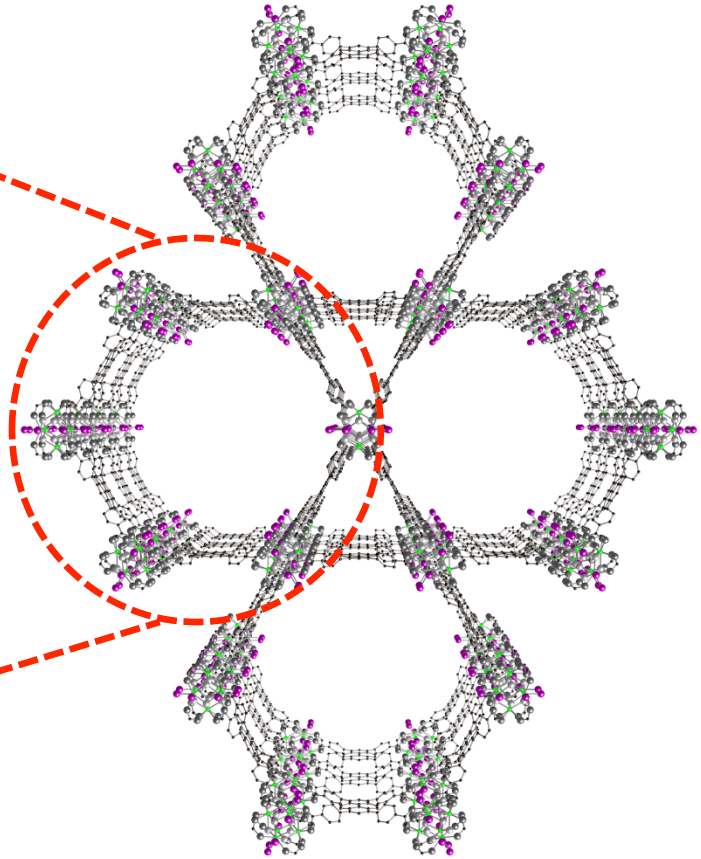
Mondloch, Bury

NU-1000









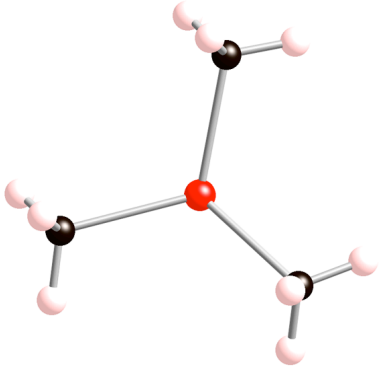
31 Å pore diameter

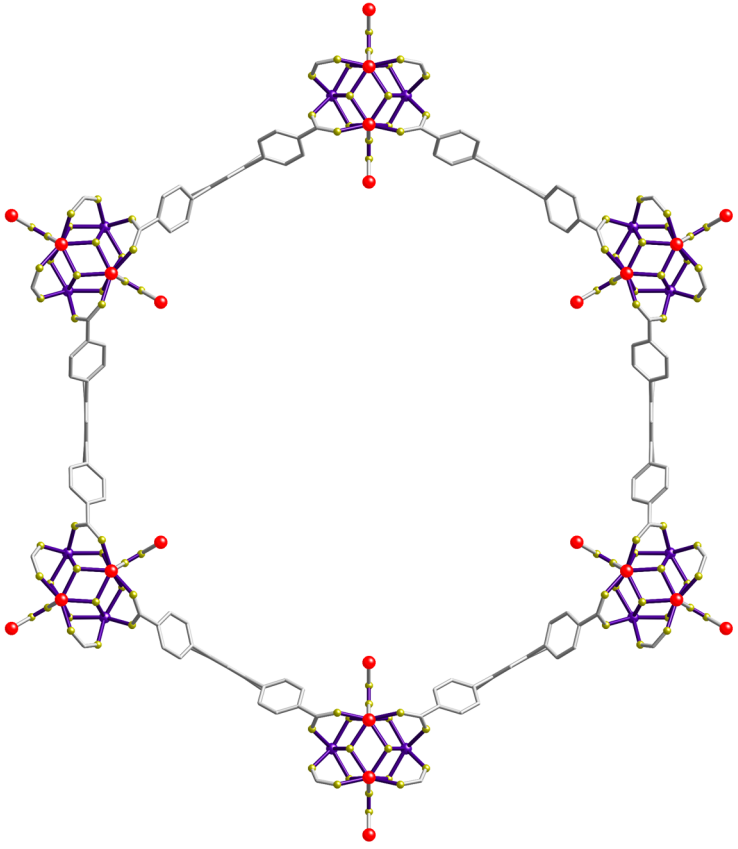
Exceptionally stable: purified by heating 80°C for 24 hours in 0.5 M HCl in DMF

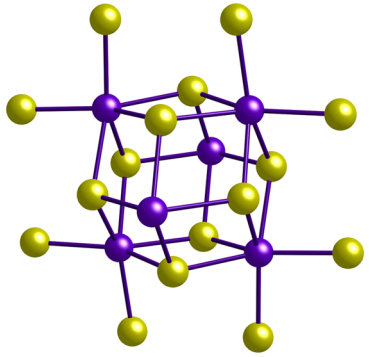
Bury, Mondloch, Timothy Wang

ICP-OES Metallation Results

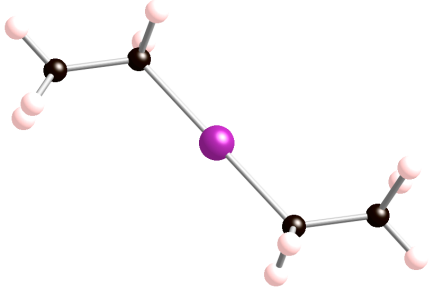
Al-AIM (Al:Zr_6 = 8)





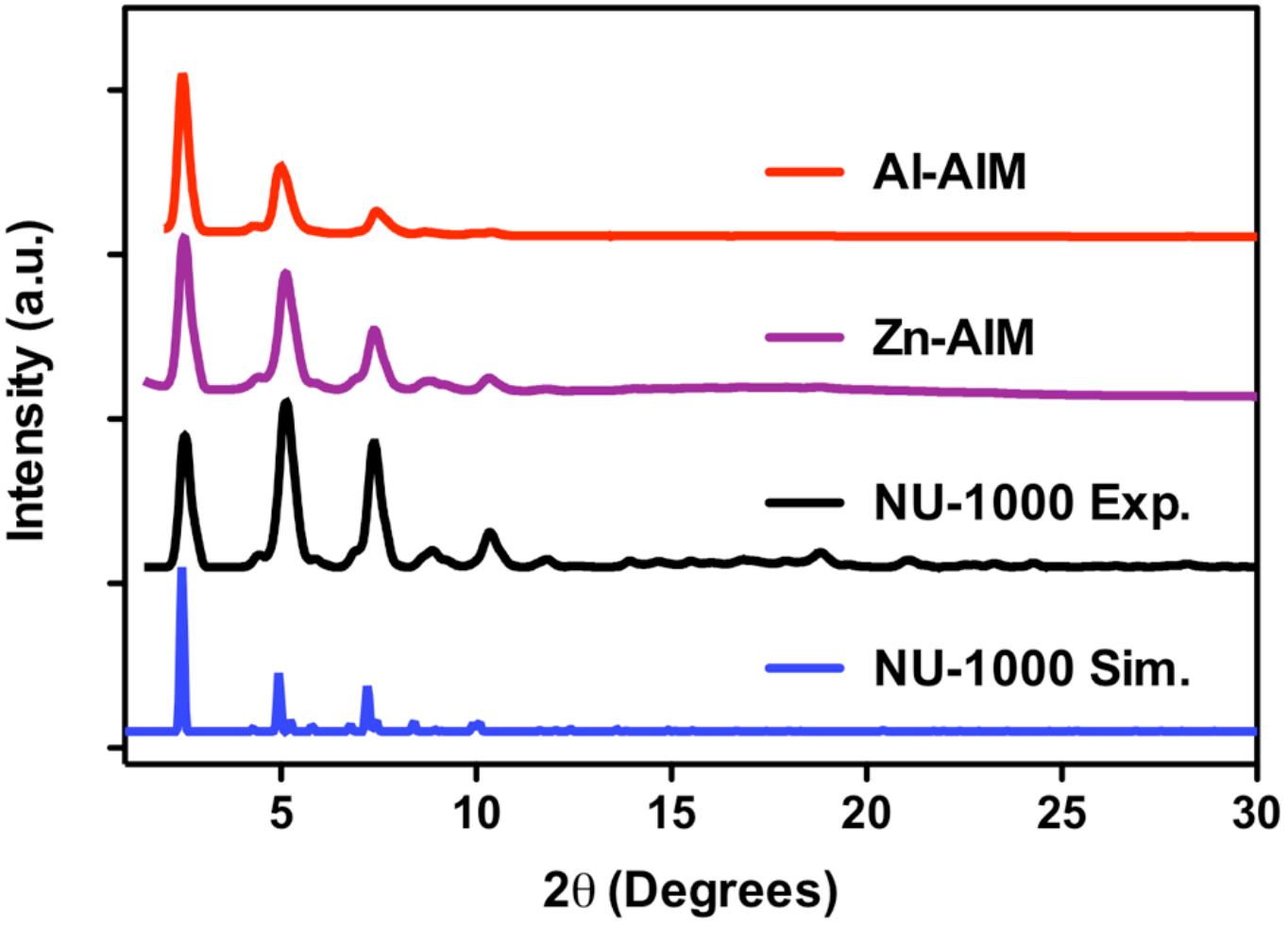


Zn-AIM (Zn:Zr_6 = 4)



Mondloch, J.E.; Bury, W. et al. *J. Am. Chem. Soc.* **2013,** *135,* 10294.

Retention of Crystallinity Following AIM: Powder X-ray Diffraction Measurements



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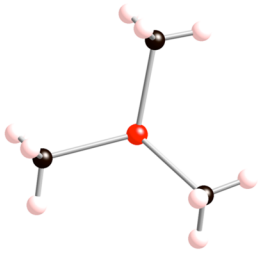
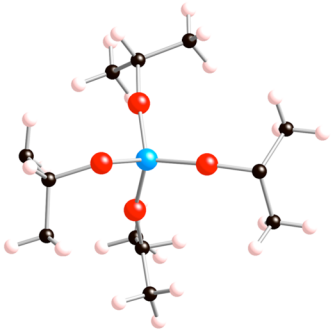
Bringing Other Metals into NU-1000

[Al-TMA]



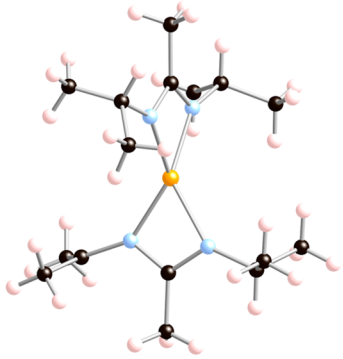
M:Zr_6 = 8

[Ti-TTIP]



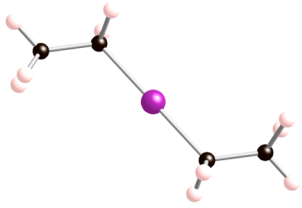
M:Zr_6 = 4

[$Ni(amd)_2$]



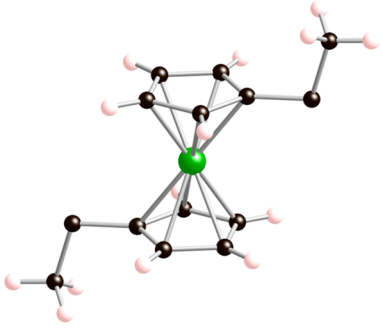
M:Zr_6 = 2

[Zn-DEZ]



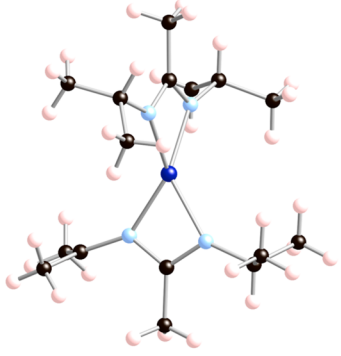
M:Zr_6 = 3

[$Mn(CpEt)_2$]

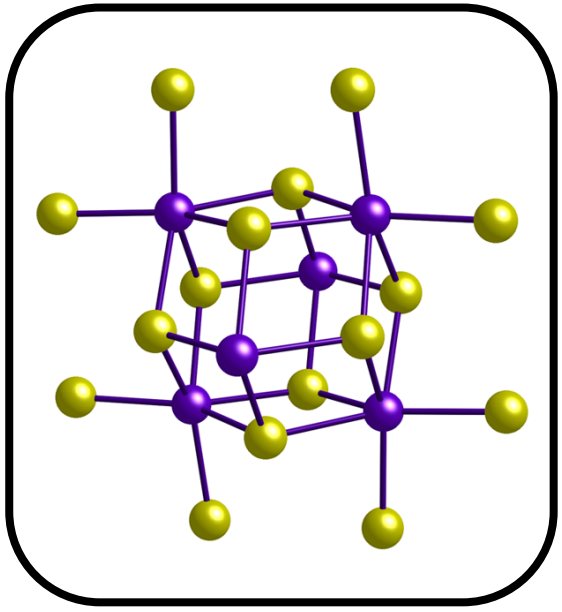


M:Zr_6 = 4

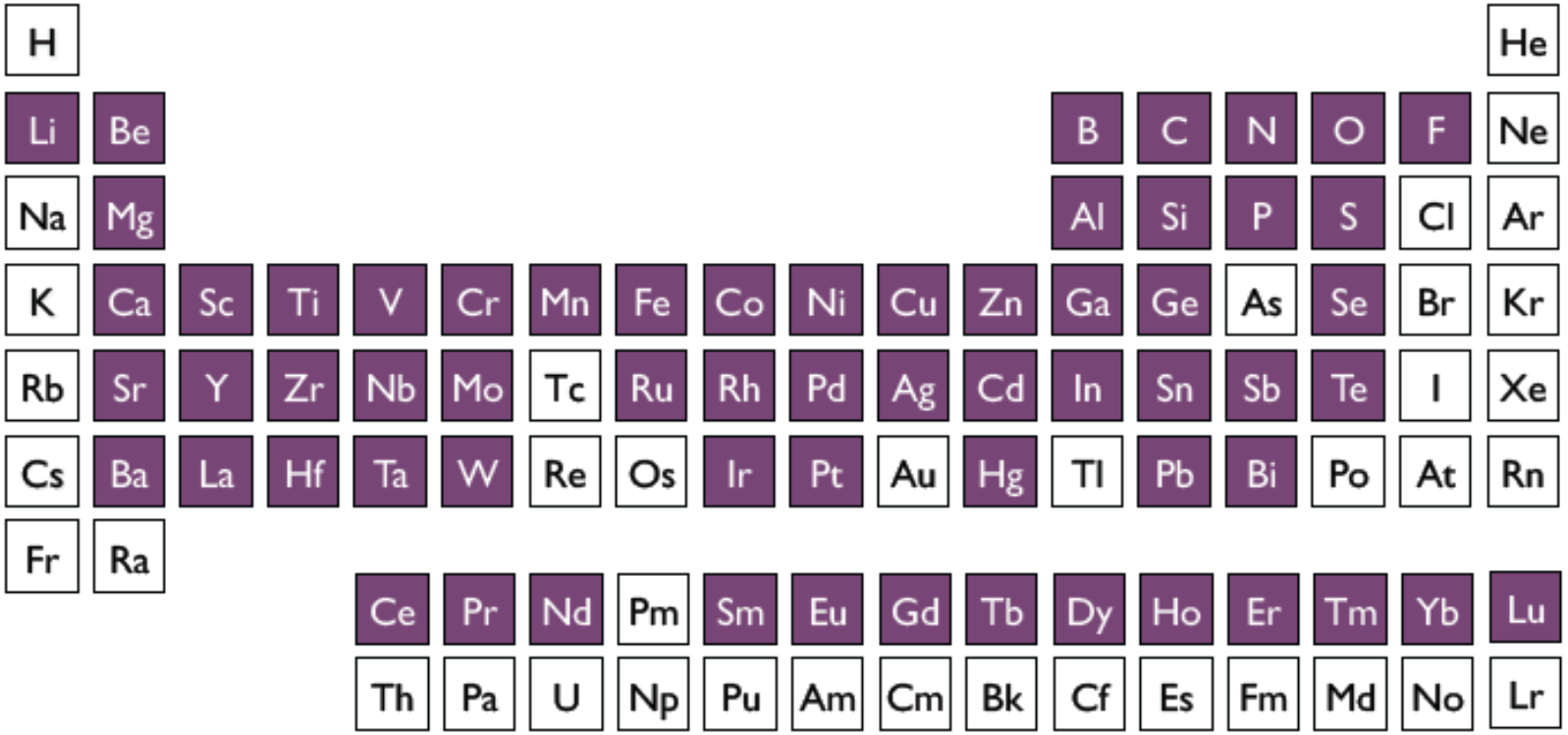
[$Co(amd)_2$]



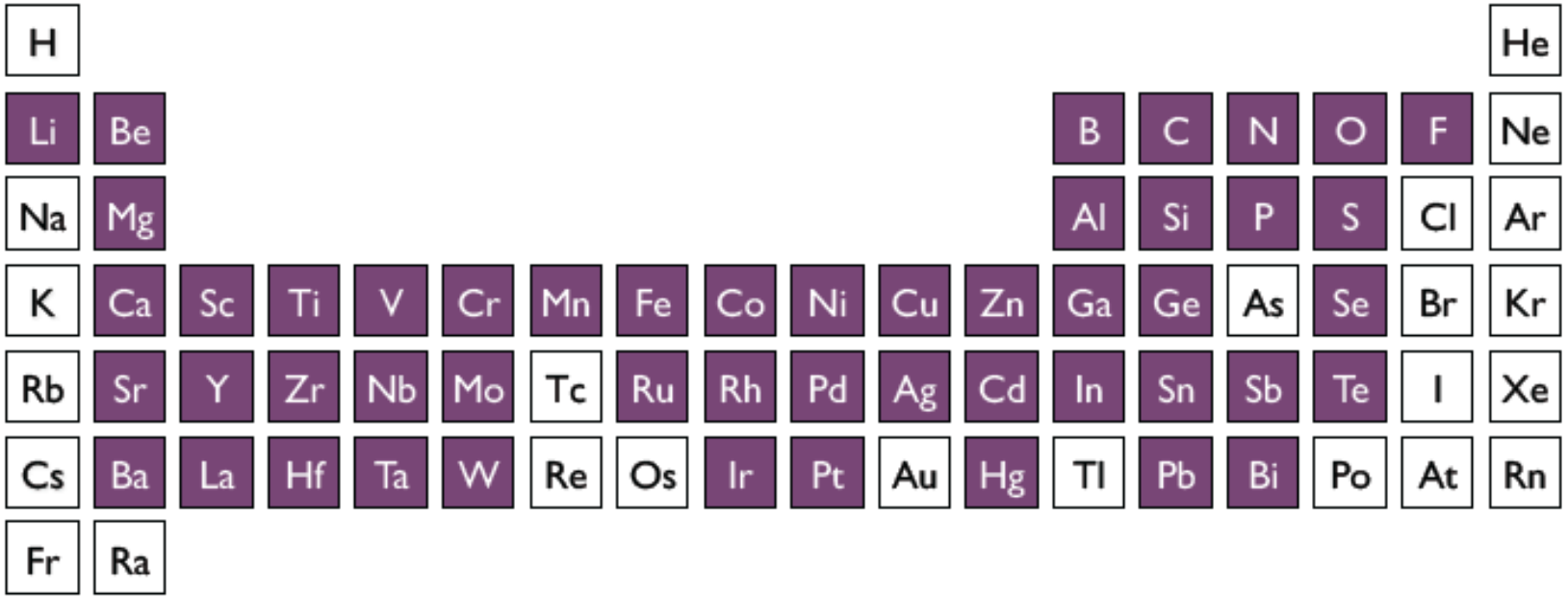
M:Zr_6 = 2



ALD Periodic Table of the Elements



Initial Success with AIM



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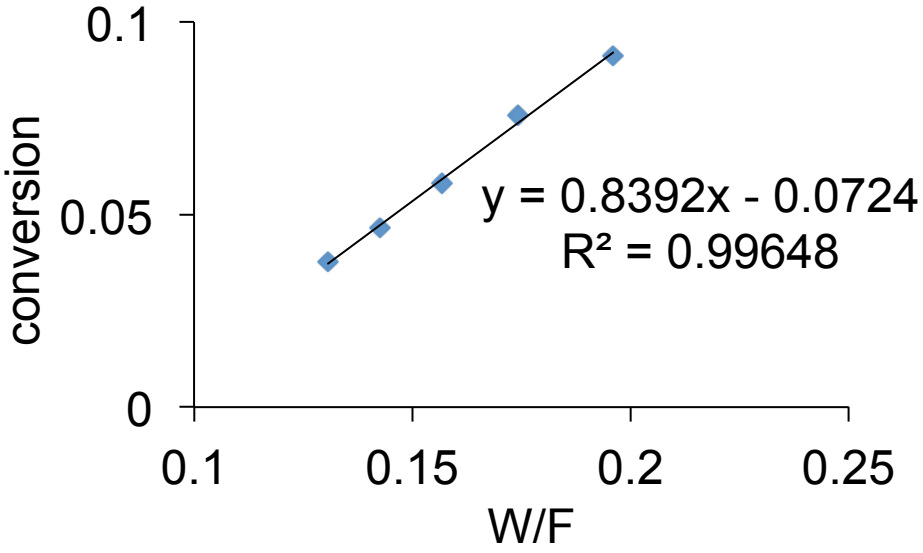
Ethylene Hydrogenation in Gas Phase

The as-synthesized Ni-AIM is not active, but H_2 treatment for 2 hours at 200 °C can activate the catalyst.

1. Pressure 1.5 bar
2. Temperature 50 °C
3. Ni-AIM 3.3 mg
4. Ethylene: H_2 1:2



- Activity: On average, TOF = 0.90 ± 0.25 s^{-1}, comparable to/slightly lower than supported Pt catalysts based on different reports
- Stability: 100% conversion of ethylene for two-week consecutive run, no decrease in activity
- Recyclability: Expose to ambient condition deactivate the catalyst, but further H_2 treatment can re-activate Ni-AIM, 100% conversion of ethylene for another week before the experiment is stopped

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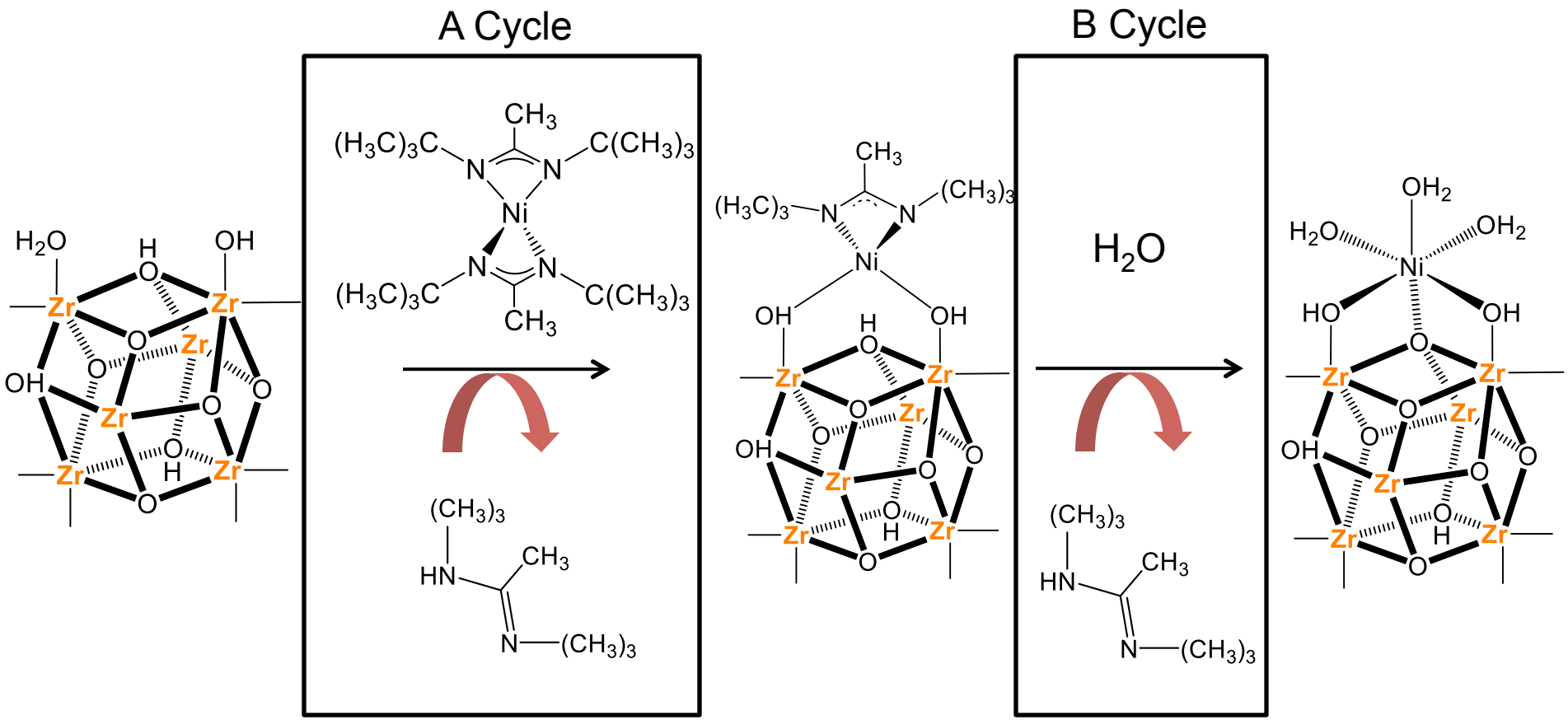
Putative Schematic Representation for Ni-AIM Process



Structural information of AIM products can be obtained through pair distribution function and extended X-ray absorption fine structure (EXAFS) analysis.

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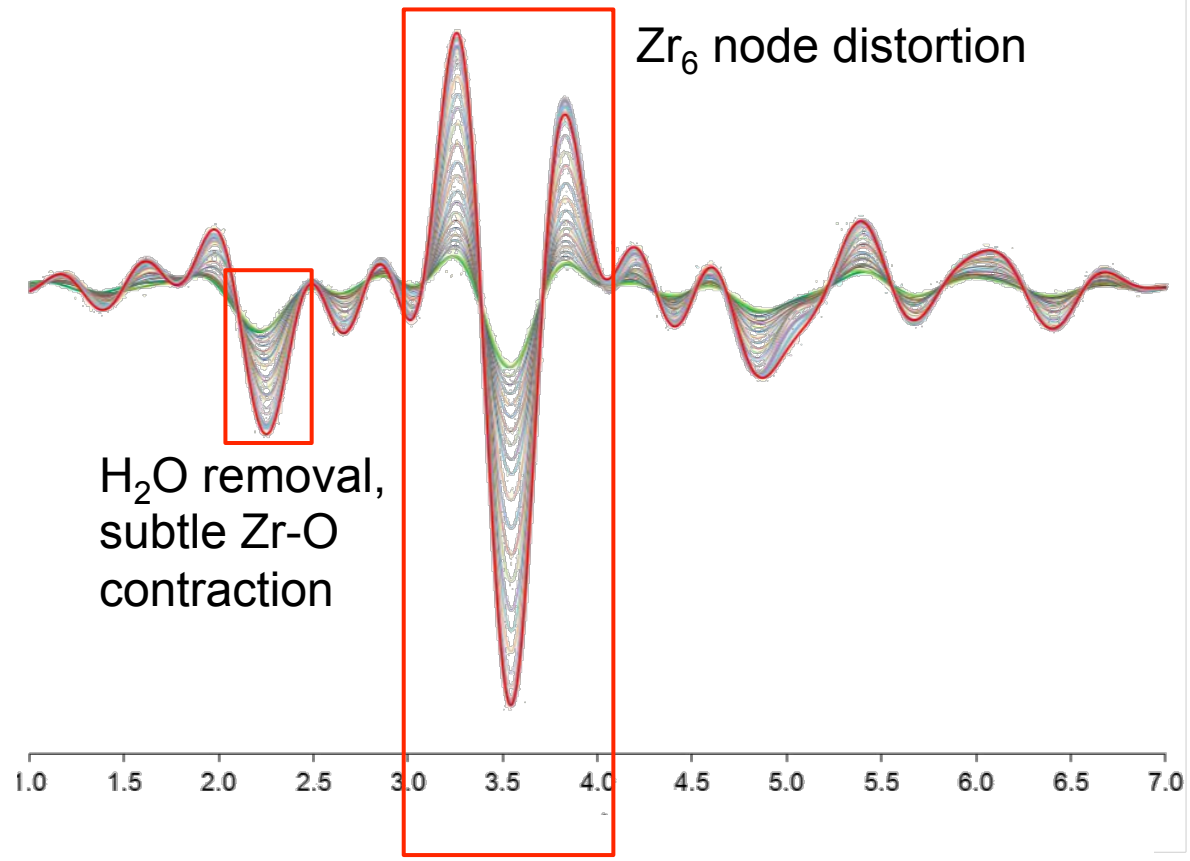
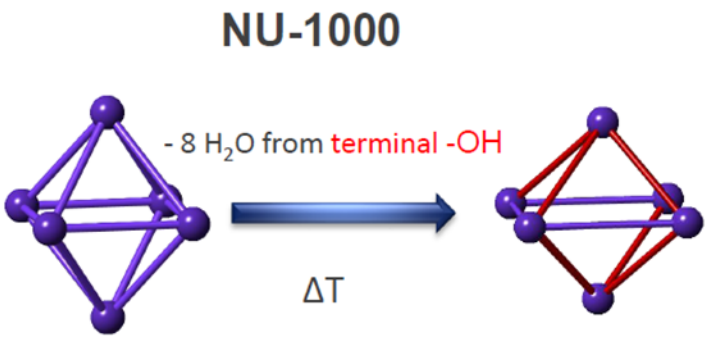
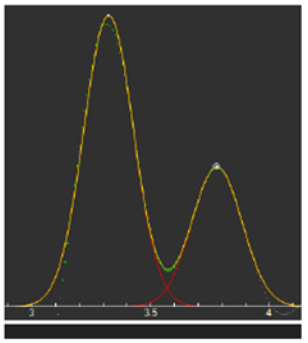
Differential Pair Distribution Function Analysis on NU-1000 upon Heating

Karena Chapman





8 d_2 Zr-Zr distances ($d_2 < d_1$)
4 d_3 Zr-Zr distances ($d_3 > d_1$)



2:1 *intensity (abundance) ratio*
short *:* ***long*** *Zr-Zr distances*

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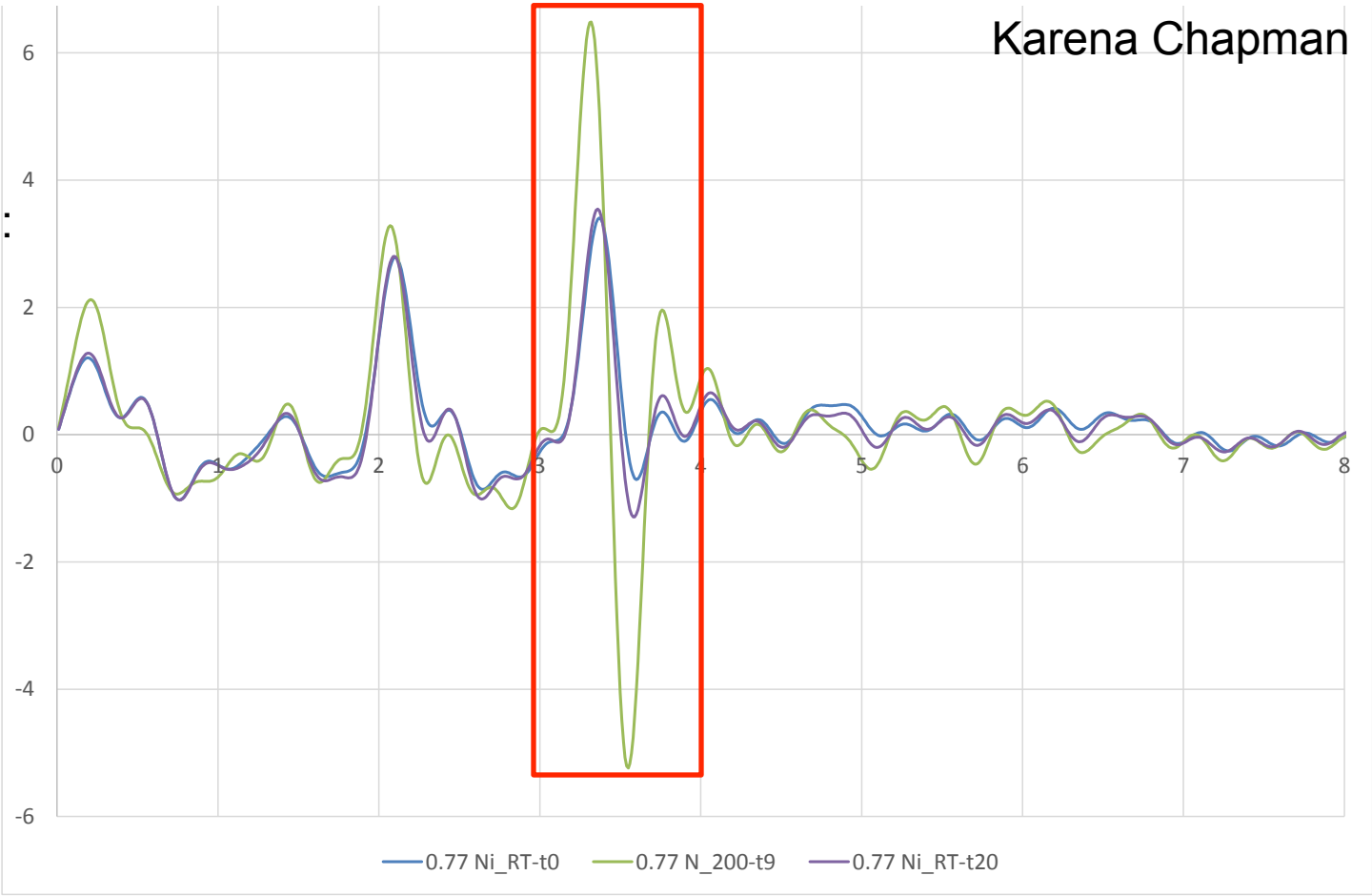
In-situ D-PDF Analysis on Ni-AIM

Karena Chapman

Gas atmosphere:
3.5% H_2 in He
Temperature program:
heat to 200°C in 1 hr
heat at 200°C in 2 hr
cool to 50°C in 1 hr
cool to RT



At 200 °C there is a large change in the structure for Ni-AIM:

- ❑ The distortions look like the Zr-node distortions we associated with dehydroxylation
- ❑ There is a contraction of the average Ni-O distance.

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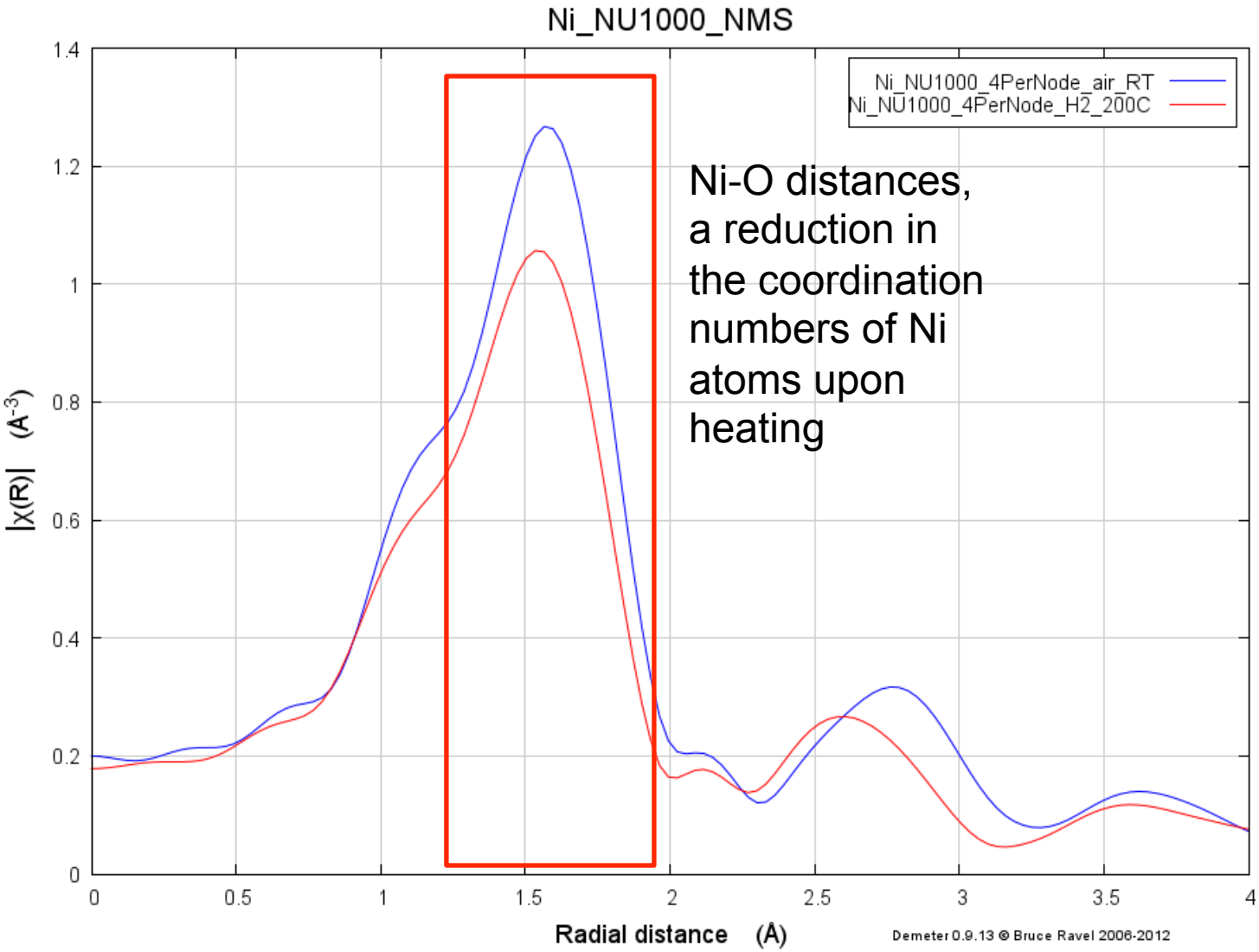
In-situ Extended X-ray Absorption Fine Structure (EXAFS)

Jeff Miller



No observation of Ni-Ni distance indicates the *single-site* nature of Ni in Ni-AIM

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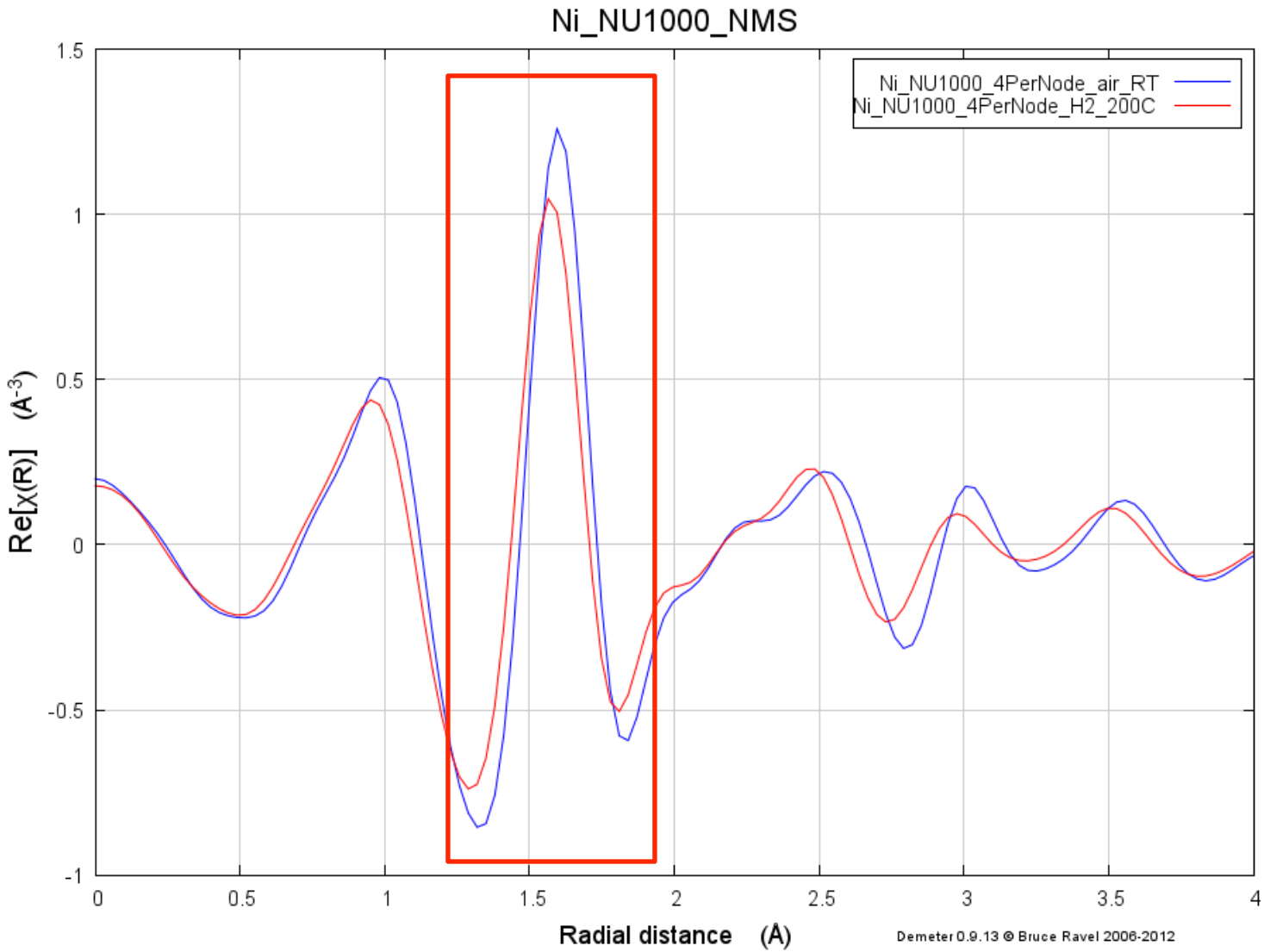
In-situ Extended X-ray Absorption Fine Structure (EXAFS)

Jeff Miller



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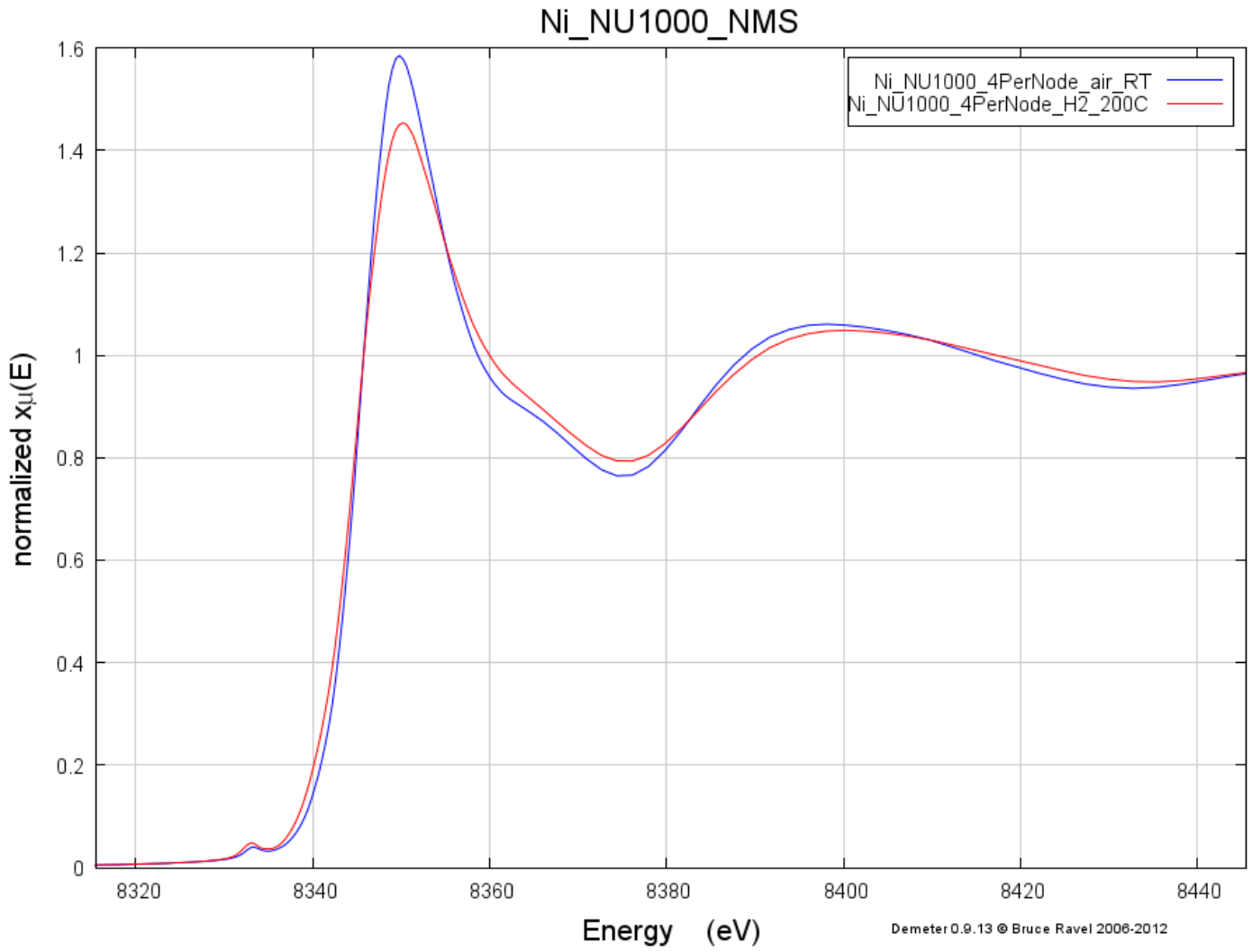
In-situ X-ray Absorption Near Edge Structure (XANES)

Jeff Miller



XANES measurements indicates the Ni(II) nature in both as-synthesized and pretreated Ni-AIM materials

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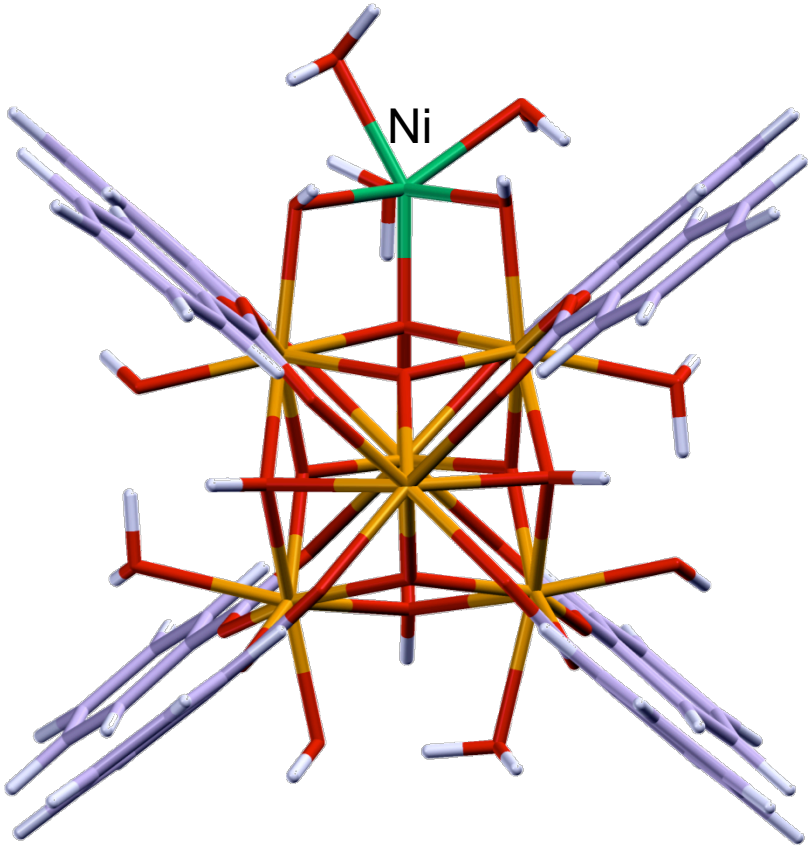
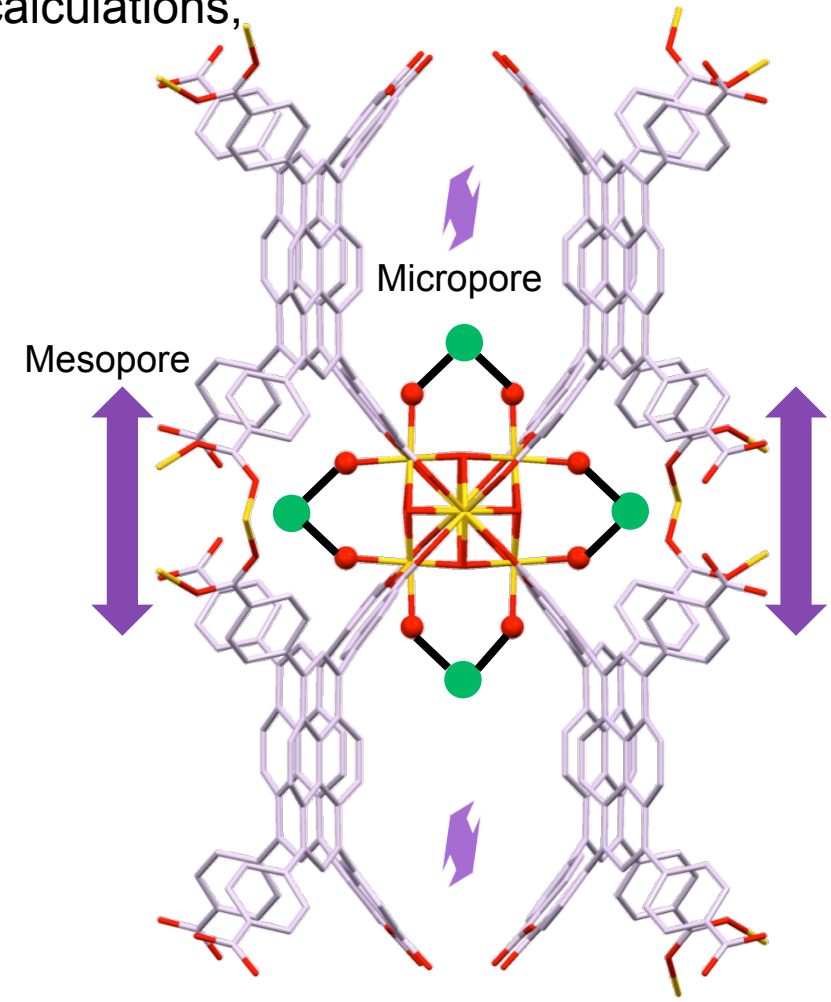
Proposed Structure of Ni-AIM

In conjunction with Density-Functional Theory calculations, this structure is proposed.





Thank you!